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MATHEMATICAL TABLES

A list of the mathematical tables now obtainable from the National Bureau of Standards is printed on pages 3 and 4 of the JOURNAL cover. New tables will be announced from time to time as they become available. An order blank is available on the last page of this issue.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1645

Part of Journal of Research of the National Bureau of Standards, Volume 34, April 1945

METHODS OF POLISHING STEEL AND THEIR EFFECTS UPON THE PROTECTIVE VALUE OF ELECTROPLATED COATINGS

By Gerald A. Lux[1] and William Blum

ABSTRACT

To determine whether the "finish" of steel prior to electroplating affects the protective value of the plated coatings, strips of cold-rolled steel were polished with wheels to which abrasives of different grain size were glued. The resultant finishes were measured with a Profilometer and were expressed as root mean square, in microinches (millionths of an inch) of the departure of the contours from a plane surface. The finishes varied from a "superfinish," with root mean square of less than 1 microinch, to 65 microinches, produced with a 90-grain abrasive. The weight (and average thickness) of steel removed by polishing was measured.

The polished specimens were plated with copper, nickel, and chromium of controlled thickness, and were exposed to the atmosphere at New York, N. Y.; Sandy Hook, N. J.; and Washington, D. C. The extent of rusting observed at periodic inspections was expressed on a numerical scale, and the average results over a period such as 1 year were expressed as "Percentage scores."

Comparison of these scores showed that wide differences in the surface finish of the steel had no significant effects on the protective value of the plated coatings. It is possible that use of hot-rolled steel, which is more likely to contain foreign inclusions, would have yielded differences as a result of polishing.

Results with accelerated tests, such as the salt spray, hot water, ferroxyl, and condensation tests, were not as reproducible and consistent as the atmospheric tests.

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[1] Formerly Research Associate of the American Electroplaters' Society at the National Bureau of Standards.

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I. INTRODUCTION

The American Electroplaters' Society has cooperated with the National Bureau of Standards in a study of the effects upon the protective value of plated coatings that result from differences in the method or degree of polishing of the metal prior to plating. The complete investigation was planned to include steel, brass, and zinc-base die castings. Thus far the work has been confined principally to the polishing and plating of cold-rolled steel and exposure of the specimens to the atmosphere in three locations. These exposure tests of the steel have been completed. As this research program has been interrupted for the duration of the war, it appears desirable to publish the results of this first phase of the study.[2]

In this report the term "polishing" is used in the restricted sense generally employed in the plating and metal finishing industries, i.e., as the removal of metal from a surface by means of abrasive particles attached by adhesive to the surface of wheels or belts. While this operation is normally applied for the purpose of making the surface smoother, it has been used in this investigation to yield any desired finish, which in a given case may be rougher than the initial surface, e.g., when cold-rolled steel is polished with a 90-grain abrasive.

As will be shown, the effects of polishing cold-rolled steel upon the protective value of the coatings, as found in this investigation, are relatively small. The detailed data obtained in the polishing operations are included because they may be of interest to persons planning a more detailed study of polishing.

II. METHODS OF DEFINING SURFACE FINISH

In order to insure that specimens polished according to a given schedule were sufficiently like each other and sufficiently different from those of another set to lead to reproducible and significant results, it was necessary to employ some objective method for defining the surface finish. Because all comparable specimens were polished by about the same procedure, except for the grain size of the abrasive, it was not necessary to select a method that fully defined the surface. It was sufficient to be able to compare the contours of surfaces similarly produced.

In 1940 the ASME issued a Proposed American Standard, B46, for surface roughness, which was revised in 1942 as a proposed "American Standard of Surface Roughness, Waviness and Lay." In it the

[2] Some of the data in this report were presented in progress reports in the Convention Proc. Am. Electroplaters' Soc. p. 54 (1941); p. 19 (1942).

FIGURE 1.—*Photomicrographic cross section perpendicular to direction of polishing, ×500.*

A, Chromium; *B*, Polished Surface; *C*, Steel. Steel specimen polished with wheel headed with 120-grain abrasive.

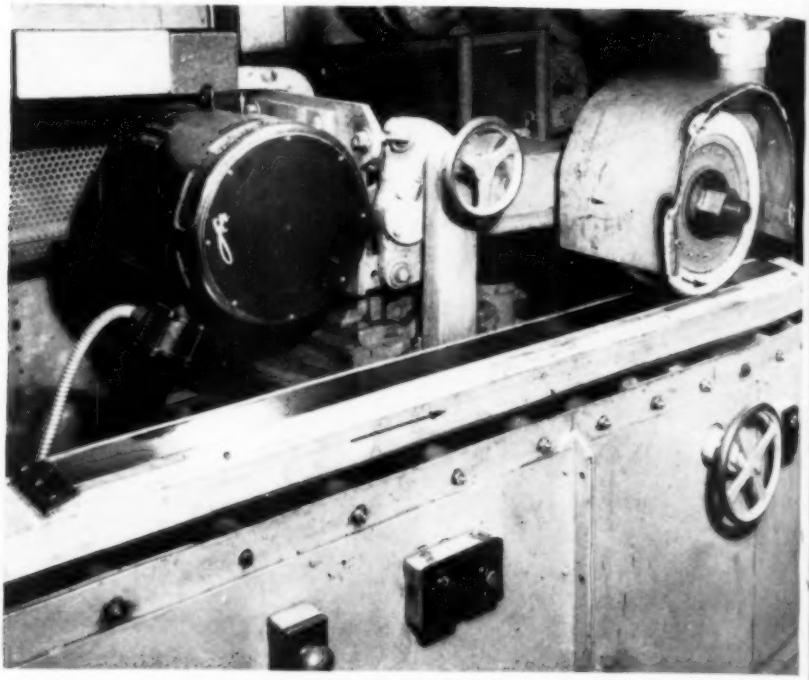

FIGURE 4.—*Polishing machine.*

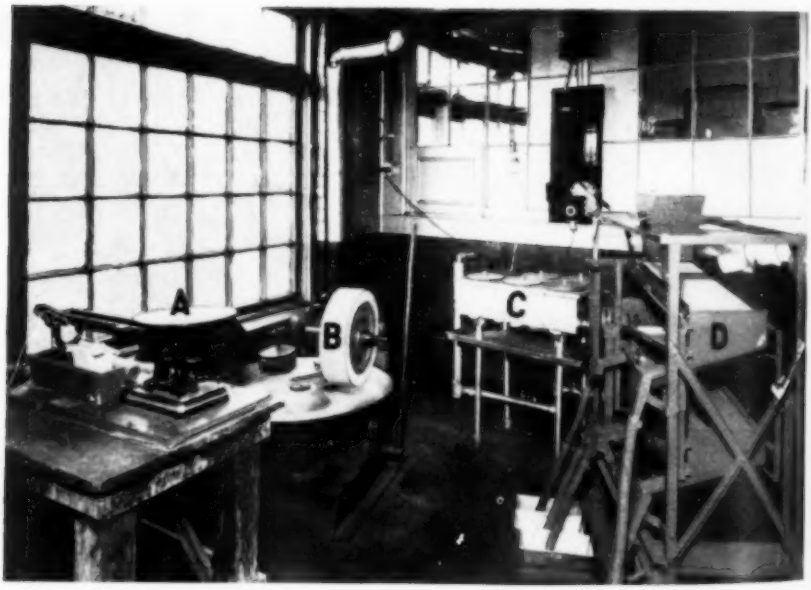

FIGURE 5.—*Equipment for preparing abrasive wheels.*

A, Scale; *B*, heading machine; *C*, glue heater; *D*, grain grader

relevant terms are defined, and a scale of roughness is based on the root mean square [3] of the height of the irregularities from the nominal surface.

Various methods have been proposed for measuring surface roughness, including (a) microscopical examination of cross sections (illustrated in fig. 1), (b) visual or photographic examination, usually with the aid of a microscope, (c) measurements of reflectivity, and (d) tracer methods. Of these, the tracer methods are most readily applied. In these methods, a fine-pointed stylus is drawn across the surface and its movements are measured or recorded. In the Brush Surface Analyser [4] this is accomplished by means of a tracing pen, the vertical fluctuations of which are usually magnified much more than

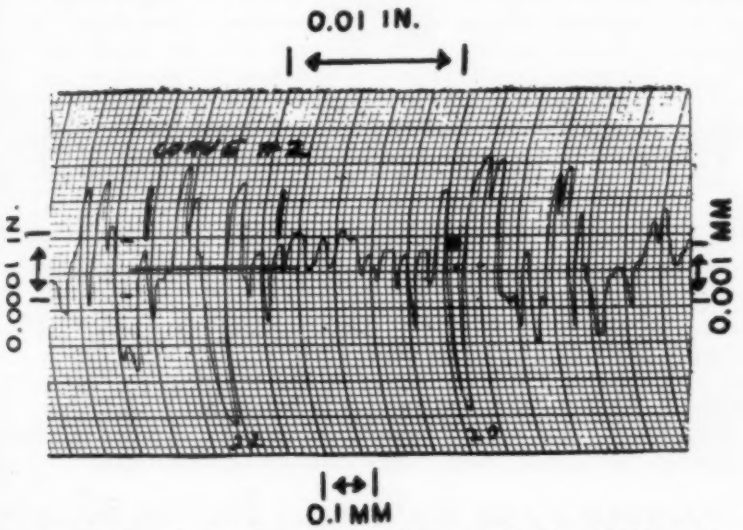

FIGURE 2.—*Brush surface analyzer chart; vertical magnification, ×3200; horizontal magnification, ×80.*

Steel specimen polished with wheel headed with 120-grain abrasive.

the horizontal. A typical curve is shown in figure 2. From figure 3, in which the Brush record and the photomicrograph are plotted on the same scale, it is evident that the tracer does not follow all the fine details of the contour.

In the Profilometer [5] the movements of the stylus are converted electrically into scale readings, the magnitude of which expresses in microinches [6] the root mean square of the deviations of the contours from a plane. If, as is frequently assumed, the contour of a polished surface followed a sine curve, the average depth of the scratches from groove to peak would be about four times the rms value. The contours on these surfaces are usually quite irregular and do not approach closely to a sine curve, but the above relation may be used as a rough guide.

[3] The root mean square (rms) of a group of numbers is the square root of the arithmetical average of the squares of the numbers.
[4] Made by the Brush Development Co., Cleveland, Ohio.
[5] Made by the Physicists Research Co., Ann Harbor, Mich.
[6] Millionths of an inch.

Each of these tracer methods has definite advantages and limitations. The Brush method yields a permanent record that is especially valuable in comparing the exact contours of surfaces. Because of the large magnification involved, this record usually covers only a short distance, e. g., 0.06 inch, and many observations are required to explore a surface. The Profilometer permits measurements over

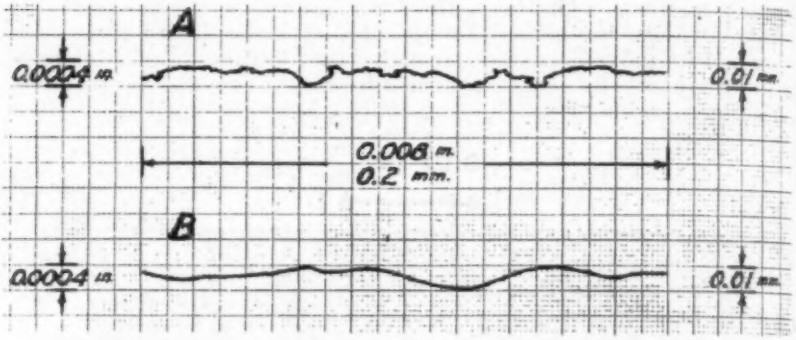

FIGURE 3.—*Comparison of profiles of adjacent areas of same specimen, both at* ×400.

A, Photomicrograph; *B*, Brush surface analyzer chart (redrawn). Steel specimen polished with wheel headed with 120-grain abrasive.

distances of several inches and directly yields numbers that serve to identify surfaces of a given type. To facilitate comparison of the finish produced at different stages in the life of a polishing wheel, systematic Profilometer measurements were made throughout this investigation.[7] The results have been used as a practical, though admittedly incomplete, definition of the polished surface.

III. MATERIALS AND EQUIPMENT USED IN POLISHING

1. MATERIALS

Steel.—The steel was a "special" SAE 1010 steel described by the manufacturer as having a cold-rolled No. 3 finish and a No. 3 temper. It was supplied in flat strips, 6 feet long, 4 inches wide, and 0.031 inch thick (No. 22 U. S. gage). To complete the study, some steel strips, 6 inches wide, from the same firm were used. This steel will be referred to as 6-inch steel. In general, the results with this steel were the same as those with the original lot.

It had a smooth, bright finish, and yielded Profilometer readings of 2 to 4 microinches. It was coated with a mineral oil and packed in oiled paper.

Polishing Grains.—The polishing grains consisted of artificial aluminum oxide, with specified grain sizes from 90 to 320, which conformed in sieving tests with the requirements of National Bureau of Standards Simplified Practice Recommendation R118–40. Roughly, a grain-size number corresponds to the number of meshes per linear inch in the sieve through which most of the grain will pass.

Glue.—This was a "ground, first run, standard emery hide glue" of the grade regularly used for "heading" polishing wheels.

[7] With the cooperation of C. B. Haven and G. M. Martin, of this Bureau.

Oil.—To produce an "oiled" finish, a mixture of 1 part of kerosine and 2 parts of medium machine oil was applied to 220 grain wheels, and a mixture of equal parts of kerosine and medium machine oil to 320 grain wheels.

Grease.—The grease finish was produced by applying tallow to the wheel, followed in some cases by a mixture of tallow and charcoal.

2. EQUIPMENT

Polishing Machine.—A straight-line semiautomatic polishing machine, figure 4, was employed. The speeds of the spindle and conveyor were adjustable, but in this study, unless otherwise noted, they were maintained respectively at 1,740 ±5 rpm and 18.5 ±0.5 ft/min. The wheel pressure was controlled by counterweights. With a wheel 4.5 inches wide, the spindle could be adjusted to provide cross polishing on the 4-inch strips up to an angle of about 10° from the direction of the conveyor belt.

Polishing Wheels.—The polishing wheels were of the compressed-canvas type and were designated by the manufacturer as having a "medium density." Each wheel was 16 inches in diameter and 4.5 inches wide. The canvas cushion was 2 inches thick, and the arbor hole was 2 inches in diameter.

Heading Machine.—The heading machine used to apply the grain to the glued wheel, shown as *B* in figure 5, had arrangements for heating the grain and for controlling the pressure of the wheel on the grain.

Glue Heater.—An electrically heated, thermostatically controlled water bath was used (*C*, figure 5).

Wheel Dresser.—A light-duty wheel-dressing machine was used to "dress," "true," and "break in" the wheels. This device is essentially a lathe that rotated the wheels at controlled speeds against the tools used for treating the wheel faces.

Wheel Balancer.—A balancing device was used to balance the wheels, and lead wire was used for adjustments.

Grain Grader.—A vibrating type grader (*D*, figure 5) with silk screens was used to "scalp" the previously used grains, that is, to remove any grain-glue agglomerates produced in previous heading operations.

Scales.—A spring scale with a capacity of 50 lb, and reading to 0.25 lb, was used to measure and control the pressure on the polishing wheel.

A beam scale (*A*, figure 5) with a total capacity of 20 kg (44 lb) and a beam capacity of 1,000 g (2.2 lb), and reading to 1 g, was used to determine the loss in weight produced by polishing a steel strip. The same scale was used to weigh the wheels and the gluepot during the heading operation.

IV. PREPARATION OF POLISHING WHEELS

The application of glue and abrasive grain to polishing wheels is commonly known as heading, and the resultant coating is called the wheel head. Before a wheel had a head of glue and grain applied to its face, it was balanced on the wheel balancer to insure smooth running in the wheel-dressing machine. To dress and true a new wheel,

it was rotated in the wheel dresser at the same speed used in polishing operations, while various tools were applied to its face to remove sufficient fabric to make the wheel cylindrical. A diamond tool, carborundum wheel-dressing stones, and sandpaper were generally used in this operation.

The wheel was then sized by brushing on a 25-percent solution of glue by weight. This treatment impregnates the canvas in the sides and face of the wheel with glue, imparts a degree of rigidity, and prevents uneven absorption of the glue subsequently applied to the face in the heading operations. A relatively high concentration of glue was used for sizing in order to reduce its penetration into the canvas and thus preserve some flexibility in the wheel. The sized wheel was allowed to dry overnight, sanded on the wheel dresser, and again sized, dried, and sanded. The wheel was then weighed.

The container, brush, and glue of a specified strength were weighed. The glue was then applied by brushing on the face of the weighed wheel. The weight of glue solution applied was considered to be the loss in weight of the container. The glued wheel face was immediately rolled into the grain in the heading machine. Excess grain was trimmed off the edges of the wheel, which was reweighed. The increase in weight represented the weight of glue solution (previously determined) plus the grain. The wheel was then allowed to dry from 15 to 45 minutes, after which other weighed layers of glue and of grain were applied. The wheel was then dried for 24 to 48 hours, depending upon the temperature and humidity. After drying, the wheel head was prepared for use by removing any high spots or rough edges by hand treatment with a carborundum stone. The wheel was then mounted on the wheel dresser and the head was broken in by slowly revolving it against a hardened steel roller at a controlled pressure. This treatment caused the glued abrasive surface to crack into segments that were smaller and more uniform than those produced by the common practice of striking the surface with a pipe. Before being mounted on the polishing machine, each wheel was again balanced. When mounted on the polishing machine each new head was run on a dummy 6-foot strip for one or more passes to remove loose grain or high spots before polishing the regular strips.

When a used wheel was reheaded with the same sized grain, the head was partly dressed off with a diamond, and the wheel was headed as above. If a different grain was to be applied, the wheel was dressed off to bare canvas and resized before heading.

The glue solutions (table 1) were prepared daily from weighed quantities of glue and of water, which were mixed and allowed to stand at room temperature for 2 hours. They were then placed in covered gluepots in the heater, and heated to 150° F (66° C), at which temperature the glue was applied to the wheels. The gluepots and brushes were cleaned and scalded daily. A special type of hydrometer, known as a gluometer, was used to check and adjust the concentration of the glue solutions at 150° F.

For the application of the grease finish, "paste" heads were used on the wheels. These were headed by applying to the dried glue sized wheel faces with a brush, two coats of a mixture by weight of 40 percent of a 19-percent-glue solution and 60 percent of a 220 grain abrasive, instead of rolling the glue-coated wheel in the grain

Two sets were polished with a proprietary greaseless aluminum-oxide preparation. This was stated by the manufacturer to be a mixture of 220 aluminum-oxide grain and a binder containing water-soluble organic compounds. The material was supplied in round bars in sealed cans. When freshly opened, it was in a moist but firm state. When applied to a revolving cloth buffing wheel, the heat of friction liquefied the binders, and the mixture was transferred to the wheel face, where it dried. Preliminary tests showed that polishing with greaseless compound did not remove as much as 0.0001 inch of steel. To make these specimens more directly comparable with the other sets, they were first polished with regular 220 grain to remove the same amount of metal as on the other comparable sets. With the greaseless compound a packed loose-muslin buff was used at 1,170 rpm.

Table 1 summarizes the data on the heading and application of wheels with various-sized grains. These represent typical conditions that were maintained in these tests, but not necessarily the best conditions for any type of commercial polishing.

V. POLISHING PROCEDURE

The steel strip was wiped with cotton and carbon tetrachloride to remove oil, weighed, and clamped at one end to a holder on the conveyor. Side guides prevented lateral motion, but permitted the strip to expand longitudinally when heated by the polishing operation. The approximate pressure during polishing was measured with the spring balance after the wheel was lowered almost to the steel surface. The pressure was adjusted by moving counterweights, which were then clamped in position, after which the scale was removed. An adjustable stop permitted the wheel face to bear fully on the steel surface, but not to touch the adjacent, slightly lower surface of the supporting wooden plank.

The wheel, running at full speed, was lowered to the stop position, and the steel strip was then passed under it. The face of the wheel traveled in the same direction as the strip. The spindle and conveyor speeds employed throughout the tests were selected as suitable after preliminary runs, but are not necessarily the most favorable. The pressure used for each grain size was governed by trial runs in which the weight of metal removed was determined and the completeness of polishing noted. During the polishing, the conveyor traveled only in one direction, and after each pass the wheel was raised and the conveyor returned to its original position. After each pass, the strip was cooled with compressed air, which also removed any loose particles of abrasive or metal. After the final pass, the strip was cleaned by brushing and was reweighed.

The losses in weight during polishing and the Profilometer readings on the polished specimens were used as criteria of the performance of a given wheel head. Whenever these losses or readings departed from those obtained during the early use of that wheel head, and especially if they approached the values yielded by wheels with the next finer grain, use of that wheel head was discontinued, even though it might have been used commercially for considerably more polishing.

Some specimens that were "superfinished" by the Chrysler Corporation yielded Profilometer values of 0.4 to 0.7 rms microinch.

VI. TYPICAL DATA AND CONCLUSIONS ON POLISHING

Typical results obtained during these polishing studies are summarized in tables 2 to 7. From these results and other observations made in this investigation, the following conclusions may be drawn regarding metal polishing under these conditions.

1. (Table 5.) The amount of metal removed in a single pass is small, and usually corresponds to an average reduction in thickness of from 0.0001 to 0.0005 inch, according to the grain size and the wheel pressure.

2. (Table 2.) Successive passes on the same steel strip during the useful life of a wheel head (for this study), with a relatively fine grain (220) and used with low pressure (18 lb) removed a fairly constant weight of metal, but the Profilometer readings gradually decreased. This decrease, observed during the life of all wheel heads used, is probably the result of the breaking down of the individual grains.

3. (Table 4.) The amount of metal removed per pass increases with the pressure. A certain minimum pressure (in this case, about 35 lb) was necessary to polish the entire surface. If the pressure is too high, the steel may be "burnt" (oxidized).

4. With continued use and repeated heading, a polishing wheel becomes more flexible, and less pressure is required to produce polishing of the entire surface.

5. With a given grain size and with given operating conditions, there is an optimum pressure with respect to (a) completeness of polishing, (b) absence of burning, (c) weight of metal removed, and (d) effective life of wheel head. The actual pressure is usually a compromise of these values.

6. (Table 4.) The polishing pressure has no significant effect on the scratch depth (Profilometer readings).

7. (Table 3.) Continued use of a wheel head in preparation of specimens was marked by a greater rate of decrease in Profilometer values than in weight of metal removed. In general, the end of the effective life of a wheel head was marked by a sharp decrease in Profilometer values rather than by a decrease in metal removed.

8. (Table 5.) The effective life of a head with a given grain size is not greatly affected by the finish of the steel prior to polishing with that head.

9. (Table 5.) Polishing with a given grain size removes about the same amount of metal per pass and yields about the same Profilometer values, regardless of the finish prior to that polishing. The average thickness of metal removed per pass was considerably more than the approximate depth of scratch with the previous coarser polish (about four times the rms Profilometer reading). In principle, nearly this amount of metal must be removed to obliterate previous scratches.

10. (Table 1.) The shorter life of heads with finer grains may be partly caused by the smaller weight of grain on their surfaces.

11. (Tables 5 and 6.) The application of oil or grease to polishing wheel heads of a given grain size materially reduces both the amount of metal removed and the Profilometer readings. With oiled wheels, a higher polishing pressure is required to remove enough metal to eliminate scratches from preceding finishes.

12. (Table 7.) The finish produced with greaseless compound was

intermediate between that made by dry, fine-grain polishing and grease polishing. It consisted of fine, discontinuous scratches, and yielded a soft matte, or satin, finish.

VII. METHODS OF PLATING

1. PREPARATION FOR PLATING

The steel specimens were examined carefully before racking to exclude any that had obvious defects. Steel racks of the type described in previous investigations [8 9] were used to hold the panels during cleaning and plating operations. In each rack six specimens are mounted in the same plane, so that there is about 0.25 inch between each edge and the adjoining panel or portion of the rack. With this spacing and a proper anode arrangement, the maximum variation from the average weight of coatings on any 12 specimens plated on 2 racks in one operation was less than ± 10 percent.

In general, the racked specimens were subjected to the following cycle of operations prior to plating: (1) Degreasing with trichloroethylene in a vapor degreaser, (2) electrolytic alkaline cleaning, (3) rinsing in water, (4) dipping in acid, and (5) rinsing in water. If the first plating was done in a cyanide-copper solution, the specimens were also dipped into a solution of 4 oz/gal of sodium cyanide, and rinsed in water. Copper-plated specimens were prepared for nickel plating by the same treatment, except that they were dipped into a solution of 4 oz/gal of sodium cyanide and rinsed in water between operations (3) and (4). Buffed nickel-plated specimen were hand-swabbed with the alkaline cleaning solution in addition to the electrolytic cleaning operation prior to chromium plating. The details of these operations were as follows.

(a) VAPOR DEGREASING

The racked specimens were subjected in a two-compartment vapor degreaser to the following cycle: (1) Immersion in boiling solvent, (2) immersion in cool distilled solvent, and (3) immersion in vapor of boiling solvent until the specimens reached the temperature of the solvent vapors, i. e., until no further condensation occurred on the rack or specimens. Stabilized trichloroethylene was used as the solvent and periodically checked for degree of alkalinity.

(b) ALKALINE CLEANING

All alkaline cleaning was done electrolytically. Cathodic and anodic cleaning and combinations of both were used. A small amount, 0.03 fl oz (1 ml), of oleic acid was added to each 50 gal of cleaning solution when prepared, to reduce formation of spray. The compositions and applications of the cleaners are listed in table 8. Originally it was intended to use but one cleaner, designated as *N* in table 8, for cleaning the specimens prior to copper or nickel plating. Because cleaner *N*, the formula used in previous investigations, did not yield satisfactory adhesion on specimens plated with bright nickel, cleaner H was substituted for that purpose. A few sets were cleaned with cleaner *C*, which had a lower silicate content than cleaner *H*.

[8] W. Blum, P. W. C. Strausser, and A. Brenner, *Protective value of nickel and chromium plating on steel*, J. Research NBS **13**, 331 (1934) RP712.
[9] W. Blum and P. W. C. Strausser, *Outdoor exposure tests of electroplated nickel and chromium coatings on steel and nonferrous metals*, J. Research NBS **24**, 443 (1940) RP1293.

(c) ACID DIPS

After alkaline cleaning and rinsing, the specimens were dipped into an acid solution until gassing occurred. The maximum time required for this action is recorded in table 9, together with the composition of all the dips and details of their use. No electrolytic pickling was done.

2. CONDITIONS USED IN PLATING

A Rochelle salt copper, a dull nickel, a proprietary bright nickel, and a chromium-plating solution were used. The compositions and operating conditions of these baths are listed in tables 10 to 13. The composition of each solution was maintained by frequent analyses and appropriate additions or adjustments.

The proprietary bright-nickel plating solution used was chosen by lot from the solutions in commercial use in 1941. It was of the organic addition agent type. Its installation, use, and control at this Bureau were under the supervision of representatives of the supplier.

3. BUFFING

All the dull-nickel and copper-plated specimens, with the exception of a few sets (indicated in tables 14 and 15), were "color-buffed" with full-disk loose buffing wheels, made from 64- to 68-thread muslin, and commercial lime-coloring compositions. None of the bright-nickel coatings required buffing. The loss in weight by buffing was determined in trial runs, and allowance was made in the thickness of plating so that the buffed deposits had the specified thickness (within ± 10 percent). The buffing losses on the nickel coatings varied from 3 to 10 percent, and on the copper coatings they were about 20 percent.

4. SCHEDULE OF DEPOSITS

The composition and preparation of the deposits are listed in table 14 for the sets exposed in September 1941, and in table 15 for the supplemental sets exposed in April 1942. To determine the effect of initial exposure at different seasons of the year and to correlate the exposure results of the two groups of specimens, reserve panels of some of the sets prepared in 1941 were exposed with those prepared in 1942. For completeness, these sets are also listed in table 15.

VIII. ATMOSPHERIC EXPOSURE TESTS

1. CONDITIONS OF EXPOSURE

In general, five specimens of each set were exposed in each of three locations. (A few sets had only three specimens of each in each location owing to inadequacy of the original steel supply.) The locations were New York, N. Y.; Sandy Hook, N. J.; and Washington, D. C. The location of the racks, their construction, and the method of mounting the specimens are the same as those previously used and described in earlier papers of this Bureau.[10]

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[10] W. Blum, P. W. C. Strausser and A. Brenner, *Corrosion-protective value of electrodeposited zinc and cadmium coatings on steel*, J. Research NBS **16**, 185 (1936) RP867. See also references given in footnotes 8 and 9.

2. METHOD OF INSPECTION AND RATING

Inspections of the specimens exposed in the fall of 1941 and in the spring of 1942 were made by the members of the AES Research Committee and other interested persons. The average number of persons at each inspection was seven.

The method of rating was described in detail in other reports (see footnotes 8, 9, 10). Each inspector assigned to each specimen a numerical rating from 0 to 5, based on the percentage of the surface that had failed. Because only steel specimens were included in this phase of the project and there was no marked evidence of other failures (such as cracking, peeling, or blistering), the ratings were determined solely by the area of the surface rusted. The percentage total scores for a given period represent the ratio of the average scores during that period to a perfect score, and hence correspond to the relative average protective value of the coatings for that period.

3. RESULTS OF EXPOSURE TESTS

The results of the inspections are given in tables 16 to 22, and in figures 6 and 7. In figures 6 and 7 the course of the corrosion is plotted against elapsed time for the buffed and bright nickel coatings, respectively, in the three locations. The relation between figure 6

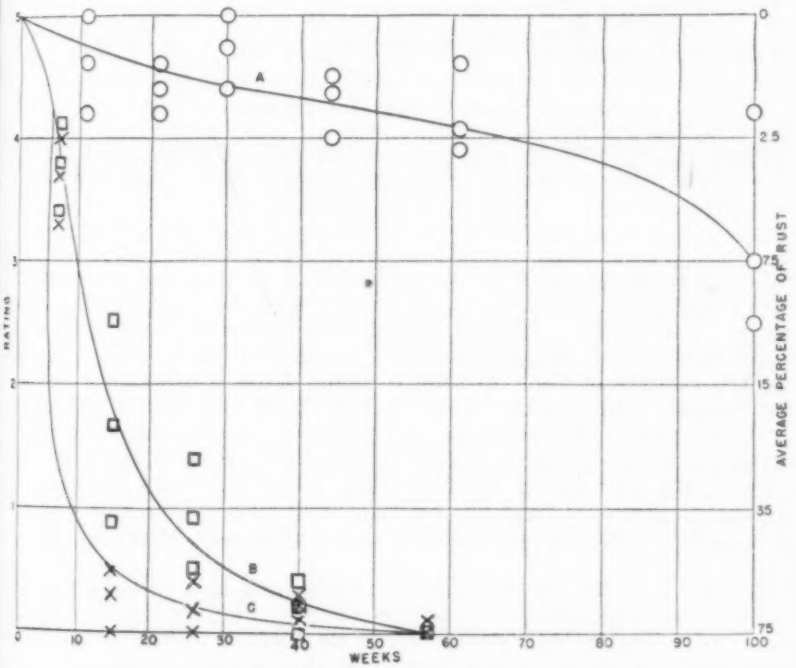

FIGURE 6.—*Rate of failure of buffed dull nickel on steel.*

All specimens were coated with 0.00075 inch of nickel and 0.00002 inch of chromium. In each location, 8 sets were exposed, on which the finish of the steel varied from 90 grain to superfinish. The three points in each location for each period represent the maximum, average and minimum ratings of the 8 sets.

Curve A. ○ Washington, D. C.
Curve B. □ New York, N. Y.
Curve C. × Sandy Hook, N. J.

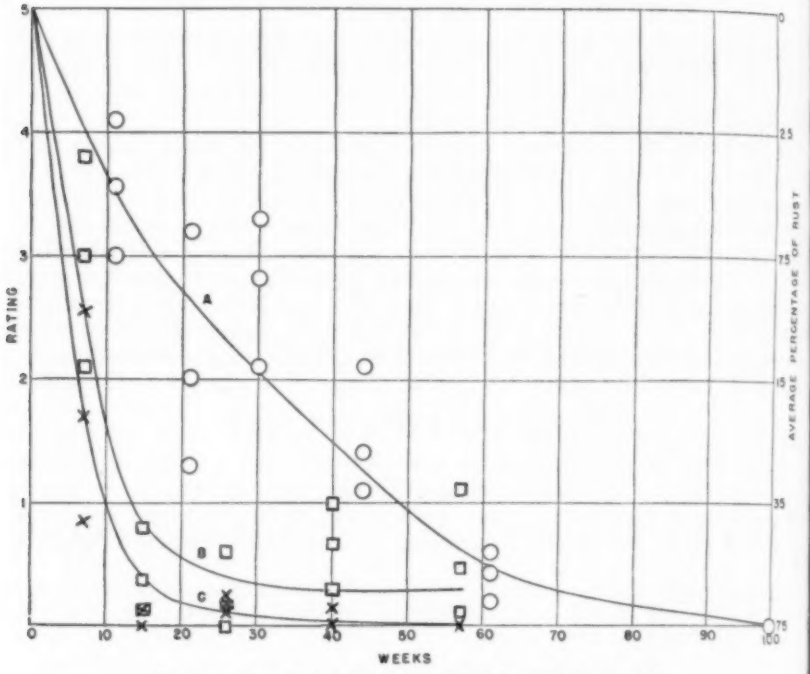

FIGURE 7.—*Rate of failure of bright nickel on steel.*

All specimens were coated with 0.00075 inch of nickel and 0.00002 inch of chromium. In each location, 8 sets were exposed, on which the finish of the steel varied from 90 grain to superfinish. The three points in each location for each period represent the maximum, average and minimum ratings of the 8 sets.

Curve A. ○ Washington, D. C.
Curve B. □ New York, N. Y.
Curve C. × Sandy Hook, N. J.

and table 16, *A*, and figure 7 and table 17, *A*, is such that each percent score in table 16, *A*, or 17, *A*, corresponds to the area under a curve drawn for that set. Instead of drawing curves for each set (which would overlap) a single smoothed curve has been drawn for the average ratings in each location. From these curves it is evident that failure is much more rapid in New York and Sandy Hook than in Washington. The extreme positions of the points with respect to each average curve show that during the course of exposure only a few of the sets varied by more than about 0.5 point in rating (or 10 percent in score) from the average, and these variations were not sufficiently consistent to indicate any systematic effect of surface finish.

In order to draw conclusions from such data, it is necessary to first evaluate the reproducibility of the results. To be significant, any effects of a particular variable must be greater than the accidental variations. A study of the results of this investigation and of the much larger number of inspection data from previous similar exposure tests indicates that in any single location a given score must vary by about 10 percent from the average of comparable sets to be significant, and for the mean of three or more locations, by at least 5 percent from the average.

When this criterion was applied to the above-mentioned tables, no

conclusive evidence was obtained of a consistent effect of the polishing upon the protective value of the plated coatings on cold-rolled steel. For example, (table 16, *A*) with 0.000 75 inch of buffed dull nickel and 0.000 01 inch of chromium, eight sets ranging from a 90-grain finish to a superfinish, showed no variations as high as 5 percent from the average of the three locations. The supplemental exposure tests (table 16, *B*) have been divided in two parts, according to the year the specimens were prepared. This distinction was made because, for no known reason, of comparable sets exposed in 1942, those plated in the first year of this project failed somewhat more rapidly than those plated later. It is not believed, however, that the former panels deteriorated in storage, as they were protected by wax paper from the surrounding atmosphere. In each group, the deviations from the average are all less than 5 percent.

With seven similar sets plated with bright nickel and chromium (table 17, *A*) there were no deviations of more than 5 percent from the average of three locations. In the supplemental tests (table 17, *B*), when divided similarly to table 16, *B*, there were some variations as high as 7 percent from the average of three locations, but these variations showed no direct relation to the preparation of the steel. No significant effects of polishing have been observed.

Comparison was also made of those sets on which the final polish was the same, but had been preceded by different prior polishing operations, which consequently removed different depths of metal from the surface. The results (tables 18 and 19) showed still smaller differences than were observed between different polishes applied directly to the steel.

No differences were observed in the behavior of specimens cut from the 4-inch and 6-inch steel strips, or of those prepared by the different cleaning procedures that yielded adherent deposits (table 21).

The results (table 22, *A*) with those few sets in which the thickness of bright nickel, or of copper plus bright nickel, was varied from 0.000 40 to 0.001 25 inch, showed a consistent increase in protective value with thickness, just as was observed in previous exposure tests.

Of those few sets (table 20) in which unbuffed dull nickel was compared with buffed nickel, the unbuffed specimens showed a marked superiority (+21%) only on the unpolished cold-rolled steel. On sets polished with 150 or 220 grain, the buffing of the nickel had no large effect.

The sets with buffed copper under bright nickel (table 22, *A*) were distinctly better (+21%) than those with bright nickel of the same total thickness applied directly to the steel; and were equal to those with buffed dull nickel of the same total thickness. This result is different from the previously reported detrimental effect of copper under buffed dull nickel. These results were confirmed with additional sets with copper followed by buffed or bright nickel that were included in the supplemental exposure tests, table 22, *B*.

4. DISCUSSION OF RESULTS

It has been generally believed that plated coatings of a given thickness are more porous and hence less protective when applied to rough surfaces than to smooth or highly polished surfaces. This belief was not borne out in these tests. Several causes may have contributed to this apparent contradiction.

1. The steel used in this study was cold-rolled and the surface was free from oxide or scale such as are normally present on hot-rolled steel. A given method or degree of polishing might not leave as continuous a metal surface on hot-rolled steel as on the steel here used.

2. This steel was of a special grade that normally contains less foreign inclusions than some other grades of steel, especially hot-rolled. It has been reported that these inclusions are more numerous below than on the surface and are therefore increasingly exposed by the successive polishing operations. No such effects were observed with the steel used in this study.

3. For most decorative plating, it is customary to produce a final bright surface. If, therefore, a deposit of nickel is applied to a relatively coarse surface, it will be necessary to "cut" and "color" the nickel to achieve a smooth, bright surface. In that process an appreciable amount of nickel may be removed from the ridges, making the coating there thinner and possibly cutting through it. Under such conditions greater porosity might be expected for coatings applied over rough surfaces than over smooth. In this investigation no attempt was made to smooth the nickel surfaces by cutting down. The slight color-buffing that was applied to the dull-nickel deposits did not eliminate the scratches derived from the base metal or appreciably reduce the thickness of the nickel, even locally.

The most similar study to this one is that described by W. L. Pinner.[11] He polished panels of (a) hot-rolled SAE steel 1085, (b) commercial cold-rolled SAE steel 1010, and (c) "perfect" cold-rolled steel 1010, with various abrasive grains, plated them with nickel, and subjected them to the salt-spray test.

With the hot-rolled steel (a) and the commercial cold-rolled steel (b) he found that a decrease in grain size of the abrasive, e. g., from 90 to 220 grain, improved the protective value of the nickel coatings. This effect was most marked when greased wheels were used for the final polish. With the perfect cold-rolled steel, no effect of grain size was observed by him except with 90 grain, which yielded a poorly protective coating.

The results of Pinner on the perfect steel are consistent with those of this investigation, except for the low rating with the 90-grain abrasive. This small discrepancy may involve the use of the salt spray in Pinner's tests, and of atmospheric exposure in the present tests. It is possibly significant that in table 16, with buffed dull nickel, the 90-grain specimens showed the average behavior in the atmosphere, but a very much larger number of rust spots in the salt spray than did other sets in this table.

The conclusions of W. M. Phillips [12] and of A. W. Hothersall and R. A. F. Hammond [13] that roughly polished surfaces yield more porous deposits, may also have involved more inclusions in their steel than were in the steel used in this study.

The conclusions reached in this study, that wide variations in the polishing operations and in the contours of the steel surface prior to plating have no significant effect on the protective value of the plated coatings, may therefore apply only to steel that is initially free from scale and inclusions and that has not been polished to pro-

[11] Convention Proc. Am. Electroplaters' Soc. p. 137 (1940).
[12] Conv. Proc. Am. Electroplaters' Soc. p. 249 (1936).
[13] Trans. Electrochemical Soc. 73, 449 (1938).

duce a smooth surface after plating. More extensive studies are required to determine the effects of polishing under other conditions.

IX. ACCELERATED-CORROSION AND POROSITY TESTS

In general, the purpose of accelerated-corrosion tests of coated metals is to determine in a short time the *relative* protective value of two or more coatings. In order to expedite corrosion some conditions of the test, such as the corroding medium or the temperature, must be different from those in the normal or expected conditions of service. Because of such variations, the actual results of the exposure test do not usually approach closely to those obtained in service. If, through research or experience, a correlation has been found between a given type of service and the results of an accelerated test, the latter may be used in research or in specifications relating to similar conditions of exposure. The exposure tests discussed above gave an opportunity to compare accelerated tests with atmosphere tests.

The failure of coatings of noble metals, including copper and nickel on steel, is associated with porosity of the coatings. It has been shown that the most effective means of decreasing the porosity is to increase the thickness. The usual porosity tests involve application of a reagent that will not attack the coating but will attack the base metal and yield visible evidence of such attack. Four such methods, namely, salt-spray, ferroxyl, hot-water, and moisture-condensation tests, were applied in this investigation to reserve specimens of the sets subjected to exposure tests. The results may be summarized as follows:

1. SALT-SPRAY TEST

This test was conducted with a 20-percent solution of sodium chloride at 95° F. in the box designed and used at this Bureau. The specimens were hung vertically,[14] and their positions were changed every 24 hours to eliminate any effects of possible nonuniform distribution of the fog. (Owing to the limited supply of the plated specimens, usually only a few of each set were subjected to each type of test.) Inspections were made and the numbers of rust spots were recorded at 24-hour intervals.

It was found that the results of the salt-spray test were not nearly as reproducible as the exposure tests of similar specimens. In the latter tests there were few sets of five samples in which there was any large deviation in the extent of rust on individual specimens. In the salt-spray test, however, at the end of 100 hours, 1 specimen might show 30 to 40 rust spots and 2 others of that set only 1 or 2 spots.

In addition, it was found that when the salt-spray test was applied to these specimens for 336 hours (14 days) most of them showed a large increase in the number of spots, in some cases to 100 or more per specimen, although some showed practically no spots after the long exposure.

This behavior suggested that the salt spray was slowly attacking the coatings and producing pores where none existed previously (just

[14] Since these tests were conducted, it has been found that more significant results are usually obtained in the salt spray by mounting the specimens at an angle, such as 15°, from vertical. These tests were conducted without the control of fog that is now specified.

as has been reported for the ferroxyl test). At first, this possibility was discounted by experiments made at this Bureau some years ago, from which it was then concluded that the rate of attack of nickel in the salt spray is negligible.

As a further check, weighed pieces of detached nickel foil, deposited respectively from the dull and the bright-nickel baths, were exposed to the salt spray for 8 days. The dull nickel acquired some brown stains and the bright nickel some green stains. These were cleaned off by light rubbing with magnesium oxide and the specimens were dried and weighed. The loss in weight of the dull nickel corresponded to 0.0020 g/dm² of exposed surface, and of the bright nickel to 0.0076 g/dm². If these losses had represented uniform attack of the entire surface, and if the foil had been 0.001 inch (0.025 mm) thick, the loss in 8 days would have corresponded to about 1/1000 of the weight of the dull nickel, or to 1/250 of that of the bright nickel. With attack on only one side (as occurs with an adherent deposit), it would have required 16,000 days (over 40 years) to completely dissolve the dull nickel and about 10 years to dissolve the bright nickel. This slow rate justifies the former conclusion that the total attack of nickel in the salt spray is negligible.

Examination of the corroded foils showed that they had not been uniformly attacked, but that numerous fine holes had been produced in the foils, which by visual examination, were apparently free from pores before the test. This behavior, which is similar to that observed with nickel in contact with ferricyanide (ferroxyl test) or with iodine, is a definite evidence that an apparently dense nickel deposit may not be homogeneous. The holes may have been produced by solution of a very thin film of nickel that had bridged over pores that were present during the initial stages of deposition. Another possibility, confirmed by a few microscopic observations, is that the deposits may contain inclusions of basic salts, which are dissolved out by certain reagents.

These results cast doubt upon the value of the salt-spray test for detecting pores in nickel coatings. Pending more exhaustive study, it is logical to take as a tentative measure of porosity the results of a relatively short period, such as 100 hours, in the salt-spray test. When this criterion was applied to the results with the polished and plated specimens, no correlation was found with the exposure tests. The two sets of dull nickel that showed large numbers (40 and 20) of spots in the salt spray, and the one of bright nickel (30 spots) were from sets that showed no marked failure in the exposure tests.

2. FERROXYL TEST

Because it had been shown by numerous investigators that the ferricyanide reagent commonly employed in the ferroxyl test attacks the nickel and produces pores, P. W. C. Strausser [15] developed a test in which paper saturated with a solution of sodium chloride and gelatin was applied to the surface and was subsequently "developed" in a ferricyanide solution. In the present study, mostly with deposits 0.000 75 inch thick, ferroxyl tests were made with the regular method and the dilute reagent, containing 60 g/liter of sodium chloride, 0.5 g/liter of potassium ferricyanide, and 10 g/liter of agar. Specimens

[15] P. W. C. Strausser, Convention Proc. A. M. Electroplaters' Soc. p. 194 (1939).

from 25 sets with a wide variation in polishing and plating, showed from zero to nine spots, with an average of only about two spots per specimen. On these relatively thick coatings it is apparent that the dilute ferroxyl reagent disclosed very few if any pores in the time of the test (10 minutes). The numbers of spots showed no correlation with the exposure tests.

3. HOT-WATER TEST

In this test the plated specimens were heated for 6 hours in distilled water kept at 194° to 203° F, and then removed and allowed to dry in the air. Any visible rust spots were then recorded. To avoid attack of glass by the water, which might increase the pH of the water, a tinned-steel container was used for hot water.

As previously reported by Strausser (see footnote 15) and others, the hot-water test generally yielded smaller numbers of spots than did the salt spray or ferroxyl. On only one set were more than five spots per specimen revealed. Of three specimens of this set the numbers of spots were 0, 12, and 15, showing poor reproducibility. No correlation was found with the exposure tests.

4. MOISTURE-CONDENSATION TEST

This test was recently used at this Bureau [16] in a study of the protective value of painted coatings on steel. The specimens are cooled in air of high humidity so that moisture condenses on them for 5 hours, then allowed to stay wet for 18 hours, and finally dried for 1 hour in warm dry air. These stages constitute one 24-hour cycle. This test proved to be slower and less discriminating than the other porosity tests. In 50 days, practically no rust spots appeared on the buffed dull-nickel specimens plated directly on the steel, although some rust spots appeared on the bright-nickel deposits within about 10 days. This method does not appear to be a practical method of testing plated metals.

The authors acknowledge the cordial cooperation of their associates at the National Bureau of Standards, including Murray Berdick, American Electroplaters' Society Research Assistant; the Research Committee of the American Electroplaters' Society; other persons who assisted in the inspections, and the following firms, who supplied equipment, materials, and assistance for this investigation: Brush Development Co., Cleveland, Ohio; Physicists Research Co., Ann Arbor, Mich.; Exolon Co., Blasdell, N. Y.; Divine Bros. Co., Inc., Utica, N. Y.; Wallingford Steel Co., Wallingford, Conn.; Lea Manufacturing Co., Waterbury, Conn.; Chrysler Corporation, Detroit, Mich.; Harshaw Chemical Co., Cleveland, Ohio; Northwest Chemical Co., Detroit, Mich.; Mutual Chemical Co., New York, N. Y.; E. I. du Pont de Nemours & Co., Wilmington, Del.; Philadelphia Quartz Co., Philadelphia, Pa.; Hanson Van Winkle-Munning Co., Matawan, N. J.; and the Bell Telephone Laboratories, New York, N. Y.

[16] R. E. Pollard and W. C. Porter, NBS Report BMS44 (April 8, 1940).

TABLE 1.—*Heading and operation of wheels*

[Minimum drying time 24 hours at room temperature. All heads consisted of 2 coats of glue and grain, the latter applied with 1 light rolling and 3 pressure rollings]

Grain size	Glue, concentration by weight	Average weight of glue plus water per head	Average weight of grain per head	Drying time between first and second coats	Break-in run before use	Pressure used in polishing	Average effective polishing life of head
	Percent	*oz*	*oz*	*min*	*ft*	*lb*	*ft*
90	33	3.4	7.4	45	30	35	
120	30	2.5	6.3	45	18	30	
150	30	2.6	5.7	30	18	25	
180	25	2.4	4.4	30	12	25	
220	25	2.0	3.7	20	12	25	
320	25	1.6	3.0	15	6	25	

TABLE 2.—*Effect of successive passes of a wheel with a dry 220-grain head on one steel specimen*

[Polishing pressure, 18 lb]

Pass number	Metal removed per pass		Total thickness of metal removed at end of last pass (×.000 01 in.)	Profilometer reading (rms microinches)		
	Ounces per strip	Equivalent thickness (×.000 01 in.)		Max.	Min.	Mean
1	0.24	19	19	30	25	
2	.21	16	35	30	22	
3	.24	19	54	27	18	
4 to 8 (avg.)	.23	18	144	31	19	
9 to 18 (avg.)	.23	18	324	28	15	
Average	0.23	18				

TABLE 3.—*Effect of continued use of a wheel with a dry 150-grain head on steel specimens*

[Polishing pressure 25 lb. New strip used after every 3 passes]

Pass number from—	Average amount of metal removed per pass		Profilometer reading (rms microinches)		
	Ounces per strip	Equivalent thickness (×.000 01 in.)	Max	Min	Mean
4 to 6	0.39	31	41	30	
16 to 18	.38	30	34	26	
31 to 33	.39	31	37	25	
43 to 45	.30	24	27	18	

TABLE 4.—*Effect of pressure on polishing wheel with 90-grain head*

[Three passes per strip]

Polishing pressure	Total metal removed (×.000 01 in.)	Profilometer reading (rms microinches)			Unpolished area	
		Max	Min	Mean		
lb					*in.*[2]	*Percent*
15	86	65	50	58	5	2
25	119	60	43	52	0.5	0.2
30	127	60	43	52	.5	.2
35	144	60	44	52	0	0
40	163	62	48	55	0	0

[a] Steel "burnt" on edges during polishing.

TABLE 5.—*Summary of polished-steel specimens*

Number	Grain size in final polish	Surface finish before final polish	Polishing pressure	Number of passes per strip	Average number of 6-ft strips per wheel head	Total metal removed (×0.000 01 inch)			Profilometer values (rms microinches)		
						Max	Min	Average per pass	Max	Min	Mean
			lb								
1	90	Cold-rolled	35	2	18	110	75	46	85	44	65
2	120	90-grain	30	2	11	78	69	37	42	39	41
3	150	Cold-rolled	25	3	7	108	83	32	37	26	32
4	150	90-grain	25	3	5	108	78	31	28	21	25
5	150	120-grain	25	3	5	94	86	30	29	23	26
6	180	150-grain	25	3	6	102	75	30	36	24	30
7	220	Cold-rolled	25	3	4	91	64	26	28	19	24
8	220	90-grain	25	3	4	89	61	25	28	19	24
9	220	150-grain	25	3	4	89	72	27	28	17	23
10	220	180-grain	25	3	4	86	55	24	24	21	23
11	320	Cold-rolled	25	3	2	72	39	19	19	12	16
12	320	220-grain	25	3	2+	61	30	15	17	10	14
13	Oiled 220	Dry 220-grain	45	3	6	22	11	6	16	12	14
14	Oiled 320	Dry 320-grain	40	3	3	19	11	5	11	6	9

TABLE 6.—*Summary of operations on the grease-polished specimens*

Operation number	Wheel head	Direction of polishing	Lubricant	Surface finish before final polish	Polishing pressure	Number of passes per strip	Total metal removed (×0.000 01 inch)			Average per pass	Profilometer value (rms microinches)		
							Max	Min	Average		Max	Min	Mean
					lb								
1	Rolled 220	Cross	None	Cold-rolled	25	3	83	72	78	26	22	14	18
2	do	Straight	Oil and kerosine	Dry 220	30	3	30	14	22	7	17	10	14
3	Paste 220	do	Tallow	Oiled 220	35	3	25	11	18	6	10	6	8
4	Paste 220, flint stoned	do	Tallow and charcoal	Grease 220	30	2	3				9	5	7
				Total		11	141	97	118				

TABLE 7.—*Summary of operations on specimens finished with a "greaseless" aluminum-oxide compound*

Operation number	Surface finish	Previous surface finish	Polishing pressure	Number of passes per strip	Total metal removed (×0.000 01 inch)				Profilometer values (rms microinches)		
					Max	Min	Average	Average per pass	Max	Min	Mean
			lb								
1	Dry 220	Cold-rolled	25	3	94	72	83	28	26	21	24
2	Greaseless Al_2O_3, grade C.	Dry 220	35	2	6	3	4	2	22	16	19
		Total			100	75	87				

TABLE 8.—*Electrolytic alkaline cleaning*

Cleaner	Base metal	Solution composition						Temperature	Current density	Time	
		Sodium hydroxide, NaOH	Sodium carbonate, Na_2CO_3	Trisodium phosphate, $Na_3PO_4.12H_2O$	Sodium pyrophosphate, $Na_4P_2O_7$	Sodium metasilicate, Na_2SiO_3	Sodium orthosilicate, Na_4SiO_4			Cathodic	Anodic
		oz/gal	*oz/gal*	*oz/gal*	*oz/gal*	*oz/gal*	*oz/gal*	*°F*	*amp/ft²*	*min*	*min*
N	Steel	0.5	4	4				195	25	2	
N_1	Copper	.5	4	4				195	25	1	
N_2	Steel	.5	4	4				195	25	2	1
Chromium	Nickel	.5	2	2				170	35	2	
H	Steel	2.0					5	195	25	2	1
H_1	Copper	2.0					5	195	25	1	
C	Steel	2.0	4		2	0.5		195	65		1
C_1	do	2.0	4		2	0.5		195	25	2	1

TABLE 9.—*Pickling*

Base metal	Preparation for deposition of	Sulfuric acid, H_2SO_4, cp, 95%; sp gr 1.84	Hydrochloric acid, HCl, cp, 35%; sp gr 1.18	Temperature	Maximum time of immersion
		fl oz/gal	*fl oz/gal*	*°F*	*Seconds*
Cold-rolled steel	Dull nickel or copper	7		120	120
Polished steel	Dull nickel	7		120	15
Copperplated steel	Dull nickel or bright nickel	7		75	15
Cold-rolled and polished steel	Bright nickel or copper		19	75	30
Buffed dull nickel on steel	Chromium	7		75	30
Bright nickel on steel	do		19	75	30

TABLE 10.—*Composition and operating conditions of Rochelle-salt copper-plating solution*

Composition	
Copper cyanide, CuCN *oz/gal*	4.0
Total sodium cyanide, NaCN *oz/gal*	5.0
Free sodium cyanide, NaCN *oz/gal*	0.8
Sodium carbonate, Na_2CO_3 *oz/gal*	4.0
Rochelle salt, $NaKC_4H_4O_6.4H_2O$ *oz/gal*	6.0
Operating conditions	
pH (glass electrode, uncorrected)	11.0
Temperature *°F*	150
Current density *amp/ft²*	20

TABLE 11.—*Composition and operating conditions of dull-nickel-plating solution*

Composition	
Nickel sulfate, $NiSO_4.7H_2O$ *oz/gal*	27
Nickel chloride, $NiCl_2.6H_2O$ *oz/gal*	6
Boric acid, H_3BO_3 *oz/gal*	4
Operating conditions	
pH (quinhydrone) at 77° F	5.0
Temperature *°F*	100
Current density *amp/ft²*	19
Cathode bar oscillated.	

TABLE 12.—*Operating conditions of bright-nickel-plating solution*

pH (quinhydrone) at 77° F	3.0
Temperature *°F*	128
Current density *amp/ft²*	25
Cathode bar oscillated.	

TABLE 13.—*Composition and operating conditions of chromium-plating solution*

Composition	
Chromic acid, CrO_3 ..... *oz/gal*	33
Sulfuric acid, H_2SO_4 ..... *oz/gal*	0.33

Operating conditions		
Plating on—	Temperature	Current density
	°F	amp/ft²
Dull nickel	110	150
Bright nickel	110	175

TABLE 14.—*Summary of preparation and plating of steel specimens exposed in September 1941*

[B = bright nickel, S = dull nickel, + = buffed. 0.000 01 inch of chromium over nickel on all specimens]

4 = 4-inch steel originally supplied.
6 = 6-inch steel supplied later when 4-inch steel was used up.
N = Original cleaner, used with direct current only.
N_1 = Original cleaner, used with direct and reverse current.
H = Harshaw cleaner, used with direct + reverse current.

Set number	Surface finish, abrasive grain size	Steel	Cleaning	Plating in 0.000 01 inch	
				Copper	Nickel
1	Cold-rolled	4	N		S 75
2	do	4	N		S 75+
2A	do	4	H		S 75+
3	do	6	H		B 75
3A	do	4	H		B 75
3B	do	6	N		B 75
4	do	6	H		B 40
4A	do	4	H		B 40
5	do	6	H	25+	B 50
5A	do	4	H	25+	B 50
5B	do	6	H	25	B 50
6	do	6	H	25+	B 100
6A	do	4	H	25+	B 100
7	90	4	N		S 75+
8	90	4	H		B 75
9	150	4	N		S 75
10	150	4	N		S 75+
11	150	4	H		B 75
12	150	4	H		B 40
13	150	4	H	25+	B 50
14	150	4	H	25+	B 100
15	90, 150	4	N		S 75+
16	90, 150	4	H		B 75
17	90, 150 cross	4	N		S 75+
18	90, 150 cross	4	H		B 75
19	90, 120, 150	4	N		S 75+
20	90, 120, 150	4	H		B 75
21	220	4	N		S 75
22	220	4	N		S 75+
23	220	4	H		B 75
24	220	4	H		B 40
25	220	4	H	25+	B 50
26	220	4	H	25+	B 100
27	220 oiled	4	N		S 75+
28	220 oiled	4	H		B 75
29	90, 220	4	N		S 75+

TABLE 14.—*Summary of preparation and plating of steel specimens exposed in September 1941*—Continued

Set number	Surface finish, abrasive grain size	Steel	Cleaning	Plating in 0.000 01 inch	
				Copper	Nickel
30	90, 220	4	H		B 75
31	150, 220	4	N		S 75+
32	150, 220	4	H		B 75
33	150, 220 cross	4	N		S 75+
34	150, 220 cross	4	H		B 75
35	150, 180, 220	4	N		S 75+
36	150, 180, 220	4	H		B 75
37	320	4	N		S 75+
38	320	4	H		B 75
39	320 oiled	4	N		S 75+
40	320 oiled	4	H		B 75
41	220, 320	4	N		S 75+
42	220, 320	4	H		B 75
43	220, 320 cross	4	N		S 75+
44	220, 320 cross	4	H		B 75
45	Superfinished	4	N		S 75+
46	do	4	H		B 75
47	Cold-rolled	6	N_3		S 75+
47A	do	4	N_3		S 75+
48	do	6	N_3		B 75

TABLE 15.—*Summary of preparation and plating of steel specimens exposed in April 1942*

[B=bright nickel, S=dull nickel, +=buffed. 0.000 01 inch of chromium over nickel on all specimens.]

4=4-inch steel originally supplied.
6=6-inch steel supplied later when 4-inch steel ran out.
N=Original project cleaner, used with direct current only.
H=Harshaw cleaner, used with direct+reverse current.
C=Low-silicate cleaner, used with reverse current only.
C_1=Low-silicate cleaner, used with direct and reverse current.

Set number	Surface finish abrasive grain size	Steel	Cleaning	Plating in 0.000 01 inch	
				Copper	Nickel
49	220 grease	6	N		S 75+
50	do	6	H		B 75+
51	Greaseless Al_2O_3	6	N		S 75+
52	do	6	H		B 75
53	Cold-rolled	6	N		S 75+
53A	do	4	N		S 75+
54	do	6	H		B 75
54A	do	4	H		B 75
55	do	6	N	25+	S 50+
56	do	6	N	50+	S 25+
57	do	6	H	50+	B 25
58	do	6	C		S 75+
58A	do	6	C_1		S 75+
59	do	6	C		B 75
59A	do	6	C_1		B 75

DUPLICATES OF ORIGINAL SETS EXPOSED IN APRIL 1942

1	Cold-rolled	4	N		S 75+
17	90, 150 cross	4	N		S 75+
43	220, 320	4	N		S 75+
1	Cold-rolled	6	H		B 75
16	90, 150	4	H		B 75
28	320	4	H		B 75
1	Cold-rolled	6	H	25+	B 50

TABLE 16.—*Effect of surface finish on protective value of buffed dull-nickel plating on steel*

[0.000 75-inch final thickness of buffed dull nickel. 0.000 01 inch of chromium]

A. PANELS EXPOSED OCTOBER 1941

Set number	Surface finish	Outdoor exposure (T=total percentage score)								Accelerated tests (spots per specimen)			
		New York (57 weeks)		Sandy Hook (57 weeks)		Washington (61 weeks)		Average of 3 locations		Salt spray 100 hr	Condensation 240 hr	Ferroxyl 10 min	Hot water 6 hr
		T	Deviation from average	T	Deviation from average	T	Deviation from average	T	Deviation from average				
2	Cold-rolled	18	0	29	+2	85	−5	43	−2	1	0	1	1
7	90	20	+2	30	+3	93	+3	48	+3	40	0	4	1
10	150	18	0	25	−2	89	−1	44	−1	6	0	4	0
22	220	17	−1	23	−4	88	−2	43	−2	0	0	3	0
27	220 oiled	19	+1	29	+2	93	+3	47	+2	0	0	2	0
37	320	21	+3	20	−7	87	−3	43	−2	20	0	0	----
39	320 oiled	19	+1	27	0	92	+2	46	+1	4	0	0	----
45	Superfinished	18	0	32	+5	89	−1	46	+1	0	0	0	----
	Average	18	±1	27	±3	90	±3	45	±2	----	----	----	----

B. PANELS EXPOSED APRIL 1942

B. PANELS EXPOSED APRIL 1942

Set number	Surface finish	Steel width	Prepared	Outdoor exposure (T=total percentage score)							
				New York (31 weeks)		Sandy Hook (31 weeks)		Washington (32 weeks)		Average of 3 locations	
				T	Deviation from average	T	Deviation from average	T	Deviation from average	T	Deviation from average
		Inches									
49	220 grease	6	1942	60	+5	64	+7	90	−2	71	+3
51	Greaseless Al_2O_3	6	1942	52	−3	60	+3	87	−5	66	−2
53	Cold-rolled	6	1942	54	−1	48	−9	94	+2	65	−3
53A	do	4	1942	52	−3	57	0	96	+4	69	+1
	Average			55	±3	57	±5	92	±3	68	±2
2	Cold-rolled	4	1941	43	−3	49	+10	90	−2	61	+2
17	90, 150 cross	4	1941	45	−1	32	−7	91	−1	56	−3
41	220, 320	4	1941	51	+5	37	−2	96	+4	61	+2
	Average			46	±3	39	±6	92	±2	59	±2

TABLE 17.—*Effect of surface finish on protective value of bright-nickel plating on steel*

[0.000 75 inch of bright nickel. 0.000 01 inch of chromium]

A. EXPOSED OCTOBER 1941

Set number	Surface finish	Outdoor exposure (T=total percentage score)								Accelerated tests (spots per specimen)			
		New York (57 weeks)		Sandy Hook (57 weeks)		Washington (61 weeks)		Average of 3 locations		Salt spray 100 hr	Condensation 240 hr	Ferroxyl 10 min	Hot water 6 hr
		T	Deviation from average	T	Deviation from average	T	Deviation from average	T	Deviation from average				
3A	Cold-rolled	20	−1	15	+4	52	+5	29	+2	3	9	0	5
8	90	24	+3	12	+1	47	0	28	+1	3	7	0	0
11	150	18	−3	10	−1	47	0	25	−2	1	1	1	0
23	220	19	−2	10	−1	46	−1	25	−2	3	8	0	1
28	220 oiled	27	+6	9	−2	56	+9	31	+4	30	9	1 to 9	1
38	320	18	−3	8	−3	42	−5	23	−4	2	6	1	0 to 15
40	320 oiled	28	+7	13	+2	49	+2	30	+3	4	2	1	----------
46	Superfinished	16	−5	12	+1	38	−9	22	−5	3	1	0	----------
	Average	21	±4	11	±2	47	±4	27	±3	----------	----------	----------	----------

B. PANELS EXPOSED APRIL 1942

D. PANELS EXPOSED APRIL 1942

Set number	Surface finish	Steel width	Prepared	Outdoor exposure (T=total percentage score)							
				New York (31 weeks)		Sandy Hook (31 weeks)		Washington (32 weeks)		Average of 3 locations	
				T	Deviation from average	T	Deviation from average	T	Deviation from average	T	Deviation from average
		Inches									
50	220 grease	6	1942	70	+5	39	+7	56	−1	55	+3
52	Greasless Al_2O_3	6	1942	55	−10	26	−6	54	−3	45	−7
54	Cold-rolled	6	1942	68	+3	25	−7	54	−3	49	−3
54A	do	4	1942	68	+3	39	+9	63	+6	57	+5
	Average			65	±5	32	±7	57	±3	52	±5
3	Cold-rolled	6	1941	45	−2	23	0	57	+11	42	−3
16	90, 150	4	1941	43	−4	23	0	37	−9	34	−5
38	320	4	1941	54	+7	23	0	44	−2	40	+1
	Average			47	±4	23	0	46	±6	39	±3

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TABLE 18.—*Effect of polishing depth on protective value of buffed dull-nickel plating on steel*

[0.000 75 inch of buffed dull nickel. 0.000 01 inch of chromium. Panels exposed October 1941]

Set number	Polishing operations	Total metal removed by polishing operations (×0.000 01 in.)	Outdoor exposure (*T*=total percentage score)							
			New York (57 weeks)		Sandy Hook (57 weeks)		Washington (61 weeks)		Average of 3 locations	
			T	Deviation from average	*T*	Deviation from average	*T*	Deviation from average	*T*	Deviation from average
10	150	96	18	0	25	+1	89	−2	44	
15	90, 150	186	20	+2	31	+5	91	+1	48	
17	90, 150 cross	194	17	−3	18	−8	87	−3	41	
19	90, 120, 150	257	19	+1	28	+2	92	+2	46	
	Average		18	±2	26	±4	90	±2	45	
22	220	78	17	−1	23	−1	88	−3	43	
29	90, 220	168	23	+5	24	0	89	0	45	
31	150, 220	177	15	−3	24	0	92	+2	44	
33	150, 220 cross	177	18	0	27	+3	91	+3	45	
35	150, 180, 220	256	19	+1	22	−2	90	0	44	
	Average		18	±2	24	±1	90	±2	44	
37	320	56	21	+2	20	−3	87	−3	43	
41	220, 320	124	21	+2	25	+2	93	+2	46	
43	220, 320 cross	124	16	−3	24	+1	92	0	44	
	Average		19	±2	23	±2	91	±2	44	

TABLE 19.—*Effect of polishing depth on protective value of bright-nickel plating on steel*

[0.000 75 inch of bright nickel. 0.000 01 inch of chromium. Panels exposed October 1941]

Set number	Average metal removed by polishing operations (×0.000 01 in.)	Surface finish	Outdoor exposure (*T*=total percentage score)							
			New York (57 weeks)		Sandy Hook (57 weeks)		Washington (61 weeks)		Average of 3 locations	
			T	Deviation from average	*T*	Deviation from average	*T*	Deviation from average	*T*	Deviation from average
11	96	150	18	0	10	−1	47	+1	25	
16	186	90, 150	19	+1	10	−1	44	−2	24	
18	194	90, 150 cross	15	−3	8	−3	43	−3	22	
20	257	90, 120, 150	20	+2	14	+3	48	+2	27	
		Average	18	±2	11	±2	46	±2	25	
23	78	220	19	−3	10	0	46	+1	25	
30	168	90, 220	26	+4	11	+1	46	+1	28	
32	177	150, 220	27	+5	9	−1	47	+2	28	
34	177	150, 220 cross	23	+1	13	+3	46	+1	27	
36	256	150, 180, 220	15	−7	8	−2	32	−7	20	
		Average	22	±4	10	±1	45	±2	26	
38	56	320	18	−6	8	−1	42	−3	23	
42	124	220, 320	28	+4	11	+2	49	+4	29	
44	124	220, 320 cross	26	+2	9	0	44	−1	26	
		Average	24	±4	9	±1	45	±2	26	

TABLE 20.—*Effect of buffing on protective value of dull-nickel plating on steel*

[0.000 01 inch of chromium over nickel. Panels exposed October 1941.]

Set number	Surface finish	Nickel plating	Outdoor exposure (T=total percentage score)							
			New York (57 weeks)		Sandy Hook (57 weeks)		Washington (61 weeks)		Average of 3 locations	
			T	Deviation from average	T	Deviation from average	T	Deviation from average	T	Deviation from average
1	Cold-rolled	S 75	47	+23	75	+35	94	+4	72	+21
2	do	S 75+	18	−6	29	−11	85	−5	44	−7
9	150	S 75	19	−5	45	+5	91	+1	52	+1
10	150	S 75+	18	−6	25	−15	89	−1	44	−7
21	220	S 75	26	+2	39	−1	94	+4	53	+2
22	220	S 75+	17	−7	23	−17	88	−2	43	−8
	Average of all		24		40		90		51	
	Average unbuffed nickel.		31		53		93		59	
	Average buffed nickel.		18		26		87		44	

TABLE 21.—*Effect of variations in cleaning on protective value of nickel plating on steel*

[0.000 75 inch final thickness of buffed dull- or bright-nickel, 0.000 01 inch of chromium. All steel, except 2", 4 inch, was cold-rolled 6-inch stock. Panels exposed April 1942.]

Set number	Cleaning	Plating	Outdoor exposure (T=total percentage score)							
			New York (31 weeks)		Sandy Hook (31 weeks)		Washington (32 weeks)		Average of 3 locations	
			T	Deviation from average	T	Deviation from average	T	Deviation from average	T	Deviation from average
53	N	S 75+	54	+2	48	−1	94	0	65	0
58	C_1	S 75+	56	+4	46	−3	96	+2	66	+1
58A	C_1	S 75+	56	+4	51	+2	95	+1	68	+3
7"	N	S 75+	43	−9	49	0	90	−4	61	−4
	Average, dull-nickel.		52	±5	49	±2	94	±2	65	±2
54	H	B 75	68	+6	25	−4	54	−2	49	0
59	C	B 75	67	+5	34	+5	54	−2	52	+3
59A	C_1	B 75	68	+6	34	+5	59	+3	54	5
3	H	B 75	45	−17	23	−6	57	+1	42	−7
	Average, bright-nickel.		62	±8	29	±5	56	±1	49	±4

TABLE 22.—*Effect of surface finish on protective value of various thicknesses of nickel with and without copper undercoat*

[0.000 01 inch of chromium]

Set number	Surface finish	Plating	Outdoor exposure (T=total percentage score)							
			New York (57 weeks)		Sandy Hook (57 weeks)		Washington (61 weeks)		Average of 3 locations	
			T	Deviation from average	T	Deviation from average	T	Deviation from average	T	Deviation from average
A. EXPOSED OCTOBER 1941										
4A	Cold-rolled	B 40	15	−1	9	+1	35	−1	20	
12	150	B 40	19	+3	8	0	38	+2	16	
24	220	B 40	15	−1	7	−1	39	−2	14	
Average			16	±2	8	±1	36	±2	15	
3A	Cold-rolled	B 75	20	+1	15	+3	52	+4	29	
11	150	B 75	18	−1	10	−2	47	−1	25	
23	220	B 75	19	0	10	−2	46	−2	25	
Average			19	±1	12	±2	48	±2	26	
5A	Cold-rolled	Cu 25+, B 50	24	−3	33	+3	83	+1	47	
13	150	Cu 25+, B 50	28	+1	27	−3	77	−5	44	
25	220	Cu 25+, B 50	30	+3	30	0	86	+4	49	
Average			27	±2	30	±2	82	±3	47	
6A	Cold-rolled	Cu 25+, B 100	50	+5	65	0	90	−2	68	
14	150	Cu 25+, B 100	46	−1	64	−1	95	+2	68	
26	220	Cu 25+, B 100	40	−5	67	+2	93	0	67	
Average			45	±4	65	±1	93	±2	68	

B. PANELS EXPOSED APRIL 1942

Set number	Plating		Outdoor exposure (T=total percentage score)							
			New York (31 weeks)		Sandy Hook (31 weeks)		Washington (32 weeks)		Average of 3 locations	
	Copper	Nickel	T	Deviation from average	T	Deviation from average	T	Deviation from average	T	Deviation from average
53		S 75+	54	+3	48	−8	94	−1	65	
55	25+	S 50+	55	+4	60	+4	99	+4	71	
56	50+	S 25+	43	−8	60	+4	92	−3	65	
Average, dull nickel			51	±5	56	±5	95	±3	67	
54		B 75	68	+10	25	−14	54	−16	49	
57	50+	B 25	64	+6	55	+16	86	+16	68	
3		B 75	45	−13	23	−16	57	−13	42	
5	25+	B 50	56	−2	54	+15	82	+12	64	
Average, bright nickel			58	±8	39	±16	70	±14	56	

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PHOTOMETER FOR LUMINESCENT MATERIALS

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ABSTRACT

In evaluating the usefulness of luminescent materials it is necessary to take into account the behavior of the human eye at low values of luminance. A photometer that provides for the determination of low luminances, with due regard for the characteristic behavior of the eye at such values, is described. It is interesting to note that both the luminescent materials and some of the phenomena of vision for the nearly dark-adapted eye have been known for many years, although the use of modern lamps to produce higher and higher illuminations has made it generally unnecessary to consider these phenomena. However, the use of the airplane for bombing with the countermeasure of blacking out as a means of passive defense and the need for markers in the interiors of blacked-out ships have shown many of the luminscent materials to be practical instead of merely novel, and has led to the development of methods for measuring the luminances they yield.

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I. INTRODUCTION

Some of the luminescent materials have been known for hundreds of years but were considered more or less as novelties until recently, when their practical usefulness became apparent. Luminescence not outlasting the excitation (fluorescence) was, in all probability, not observed until after the invention of irradiating sources and devices especially designed for the purpose of detecting such luminescence. Luminescence, such as that of glowworms and rotting wood, and that which outlasts the excitation (phosphorescence), must have been noticed by man in his early existence. Aristotle's pupil, Theophrastus, says that a carbuncle exposed to sunlight glows like a live coal,[1] and Aristotle himself (about 350 BC) mentions the luminescence of rotting wood. Benvenuto Cellini tells of seeing a white sapphire that illuminated a perfectly dark room.[2] As early as 1625 Peter Poterius made little toy animals from phosphorescent material (see footnote 1). An alchemist, Vincenzo Cascariolo, in Bologna, Italy, about 1600 found a stone which seemed heavier than one of its size should be, and upon heating it, in the hope of finding gold, he dis-

[1] P. Pringsheim and M. Vogel, Luminescence of Liquids and Solids and its Practical Applications (Interscience Publishers, Inc., New York, N. Y., 1943).
[2] S. H. Ball Sci. Monthly, p 497 (1938).

covered that it would glow in the dark, "sometimes for as long as an hour" and also found how to make it glow at will.[3]

The luminance [4] of the luminescent light from phosphorescent materials ranges downward from that of a white surface viewed in full moonlight. In measuring such luminances it is necessary to consider the behavior of the weakly illuminated eye. In 1826 J. Purkinje [5] showed that after a red surface and a blue surface have been illuminated so as to have the same brightness, a reduction of the illumination of both surfaces in the same proportion will cause the red surface to appear darker than the blue after a certain limit of reduction has been passed. The dependence of the observed values also upon the size of the field of view for the nearly dark-adapted eye was determined by P. Reeves [6] in 1917. The trend to higher and higher illumination for lighting purposes had made it unnecessary for the photometrist to remember these effects in the measurements customarily made in the laboratory. However, when the use of luminescent materials was shown to be practical it became necessary to take account of both of these phenomena in constructing a photometer for the measurement of their luminance.

II. PHOTOPIC, MESOPIC, AND SCOTOPIC VISION

The human eye has the ability to adapt for light conditions over a wide range. The approximate upper limit is represented by the condition of viewing fresh snow in full sunlight, which is uncomfortable and, if long continued, results in a temporary blindness, "snow blindness," or if viewed for prolonged periods, may result in permanent injury to the eye. The lower limit is considerably below the condition of viewing a white surface on a clear, moonless night. The change in size of the pupil of the eye is easily observed, and, as everyone knows, the pupil is small if strongly illuminated, and as the illumination weakens the pupil becomes larger. There are other less obvious changes, such as the change in the luminosity curve, which explains the Purkinje effect and the loss of the ability to detect detail (acuity) and of the ability to detect chromaticity differences, all associated with the transition from cone to rod vision.

When we view a surface of high brightness with photopic vision, that is, when the eye may be said to be light-adapted, we find that the eye has a nearly constant luminosity curve, independent of the luminance range under consideration. All definitions of units of luminance (photometric brightness) imply that comparisons between differently colored surfaces be made at values of luminance sufficiently high to insure that the observer's eye is in a state of light adaptation. This is to insure that luminance values obey the additive law, by which a luminance of y units superimposed upon one of x units will provide a luminance of $(x+y)$ units. If this law is not obeyed, the ordinary inverse square law, the ratio of areas of openings in diaphragms, and the ratio of the areas of the open and opaque sectors of a rotating disk (Talbot's law) may not be applied to the luminance values under consideration. If differently colored surfaces are viewed, obedience to the above-mentioned laws occurs only if the luminosity curve of

[3] G. T. Schmidling, Protective and Decorative Coatings, **III**, 657 (John Wiley & Sons, New York, N.Y., 1943); also reference 1.
[4] Psychophysics of color, OSA Committee on Colorimetry, J. Opt. Soc. Am. **34**, 245 (1944).
[5] J. Purkinje, Magazin gesammte Heilkunde (Berlin) **28**, 199 (1826).
[6] P. Reeves, J. Opt. Soc. Am. **1**, 148 (1917); P. G. Nutting, Trans. Illum. Eng. Soc. **XI**, 939 (1916).

the eye is constant and independent of the adaptive state of the eye throughout the range of luminance under consideration. Fortunately the eye in observing luminances greater than 1,000 microlamberts does possess a nearly constant luminosity curve, and for this condition (when the eye is said to be light-adapted) we have photopic vision and the values of luminance (photometric brightness) for differently colored surfaces not only obey the additive law but also correlate well with brightness, subjectively evaluated. We may speak of such values as photopic luminance.

Unfortunately the luminosity curve of the eye does not remain constant when the luminance of an extended surface is reduced below 1,000 microlamberts; in fact, the eye becomes progressively more

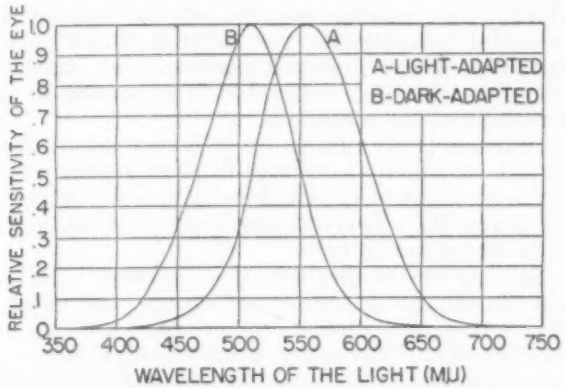

FIGURE 1.—*Comparison of the luminosity curves for the light-adapted (A) and for the dark-adapted (B) eye.*

sensitive to short-wave (blue) and less sensitive to long-wave (red) light as the luminance to which it is adapted is reduced from 1,000 to about 0.5 microlambert, the rate of change being most pronounced between 200 and 1 microlambert. This shift of the luminosity curve toward shorter wavelengths explains the Purkinje effect. For adaptation to luminances below 0.5 microlambert, the eye again reaches a steady state, with a constant luminosity curve characteristic of scotopic vision, and the eye may be regarded as dark-adapted. We may speak of these luminances as scotopic luminances. In figure 1 the adopted luminosity curve of the light-adapted [7] eye and an average curve for the dark-adapted [8] eye are shown. As the luminance of the observed surface is diminished, we pass through the region of mesopic vision, and the luminosity curve moves progressively from that of the light-adapted eye toward that of the dark-adapted.

The following are four of several ways to assign numerical values to a scale of luminance below the photopic region to include mesopic and scotopic luminance.

A. Arbitrary application of the photopic luminosity function to all luminances by making visual comparison of fluorescent and phosphor-

[7] A résumé of the data on which the standard ICI luminosity factors are based and of the present status of these factors is given in a paper by Kasson S. Gibson, *Spectral luminosity factors*, J. Opt. Soc. Am. **30**, 51 (1940).

[8] "Summary of American Opinion on BS/ARP 18, British Standard Specification for Fluorescent and Phosphorescent Paint," prepared for the American Standards Association by L. A. Jones under date of June 15, 1942, gives an average of the luminosity data for low luminances determined by Hecht and Williams and by Weaver.

escent materials only with a standard of similar spectral composition, the standard to be evaluated by way of the photopic luminosity function.

B. Adoption of an arbitrary photoelectric procedure for evaluating the radiant energy from fluorescent and phosphorescent materials.

C. Definition of the unit and scale of mesopic and scotopic luminance in terms of the hypothetical equal-energy source.

D. Definition of the unit and scale of mesopic and scotopic luminance in terms of an incandescent lamp operating at 2,360° K color temperature.

There have been attempts to make the standard photopic luminosity function (A) do. Each material characterized by radiant energy of a new spectral composition requires the setting up and evaluation of a new standard. For various samples of the same material, the method gives useful comparisons; but because of the Purkinje effect, photopic luminance of one material compared to another does not necessarily correlate with the observable brightnesses in the mesopic and scotopic regions of the materials.

A better correlation is obtainable by arbitrary adoption of a photoelectric procedure in which the source-filter-photocell combination is approximately equivalent to the luminosity function somewhere within the mesopic range (B). It is obvious, however, that no one luminosity function can be generally valid.

The lamp illuminates the flashed opal diffusing glass screen, S_1, which in turn illuminates a similar screen, S_2, the outer surface of which, viewed in the front-surface mirror, M, forms the comparison field of the photometer. The other, or test field, is the surface of the sample viewed directly. The luminance of the surface of S_2 facing the mirror depends upon the light reaching the surface toward S_1, which is closely proportional to the product of the area of the opening in the diaphragm D and the luminance of the surface of S_1 exposed to S_2, since the distance between S_1 and S_2 is constant. The luminance of the surface of S_1 away from the lamp is proportional to the illuminance of the surface toward the lamp which, of course, depends upon the distance between S_1 and the lamp.

Procedures C and D are similar and give values of mesopic and scotopic luminance that correlate well with brightness. The use (C) of the hypothetical equal-energy source would bring a unique, logical simplicity to the general concept of luminance, but the predominant opinion (see footnote 8) is that an incandescent-lamp source at 2,360° K is more convenient in practice and, on that account, preferable for tentative standardization and use at the present time. By this choice the comparison source is assigned mesopic and scotopic luminances by the same methods (inverse-square law, sector-disk relations, aperture relations) used for photopic luminance.

III. DESCRIPTION OF THE PHOTOMETER

1. PHOTOMETRIC DETAILS

The photometer is shown in figure 2. The views depart from conventional drawing practice by showing the openings in the baffles and diaphragms as in a section taken through the axis of the beam. Otherwise, figure 2 shows conventional plan and elevation views.

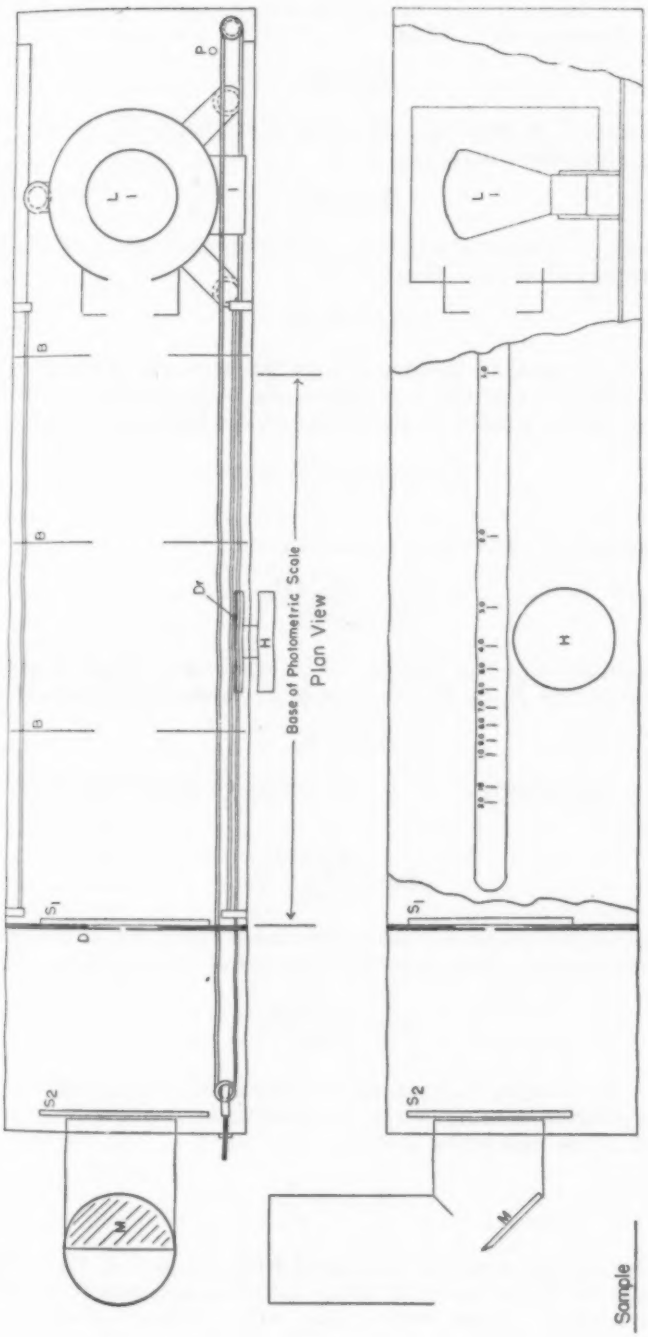

FIGURE 2.—*Photometer for luminescent materials.*

Let the luminance of M, as viewed from the sight tube, be B_M, the reflectance of the mirror be r, and the luminance of the surface of S_2 facing the mirror be B_2. Then

$$B_M = rB_2.$$

The luminance B_2 is proportional to the illuminance E_2, on the surface of S_2 away from the mirror, or

$$B_2 = k_2 E_2,$$

the constant of proportionality, k_2, being characteristic of the transmissive properties of S_2. Hence

$$B_M = rk_2 E_2.$$

However, E_2 is equal to the product of the area, A, of the opening in the diaphragm, D, and the luminance, B_1, of the surface of S_1 facing S_2, divided by the square of the distance, d_1, between S_1 and S_2,

$$E_2 = \frac{AB_1}{d_1^2}$$

and we accordingly have the expression

$$B_M = \frac{rk_2 AB_1}{d_1^2}$$

for the luminance of the mirror. The luminance B_1 is proportional to the illuminance E_1 on the surface of S_1 toward the lamp, or

$$B_1 = k_1 E_1,$$

where k_1 is characteristic of the transmissive properties of S_1, which gives us

$$B_M = \frac{rk_2 Ak_1 E_1}{d_1^2}.$$

Finally, $E_1 = (I/d^2)$, where I is the luminous intensity of the lamp, L, in the direction of S_1 and d is the distance of L from S_1, so that

$$B_M = \frac{rk_2 Ak_1 I}{d_1^2 d^2}.$$

In this we see that r, k_2, k_1, I, and d_1 are fixed characteristics of any particular photometer and can be grouped under a single characteristic, P, and hence we can write that

$$B_M = P\frac{A}{d^2}.$$

The photometric scale is graduated from 20 to 0.5, and a set of 4 diaphragms having holes with areas differing by factors of about 10 has been made.[9] These were made with ordinary drills and then

[9] Metric drills of 0.5, 1.6, 5, and 16-mm will give areas proportional to 0.25, 2.56, 25, and 256, provided new accurately ground drills are available. For some purposes these area ratios may be sufficiently close to the desired factors of 10.

calibrated. The photometric scale and the ratios of the areas of the openings in the diaphragms overlap and values near the ends of the scale can be measured by means of either of two diaphragms. The use of these mechanical means to control the luminance of the comparison field gives a long range with no change in spectral composition. When the photometer is used without any of the removable diaphragms, the maximum reading is more than 150,000 times the minimum reading with the smallest-aperture diaphragm. The opening in the metal plate holding S_1 is a limiting diaphragm when none of the removable diaphragms are used.

The field is a plain elliptical field (diametrically divided circle viewed at 45°), the major axis being 1½ inches long. The major axis coincides with the dividing line of the field, which usually is viewed so that the two halves are seen side by side. Since the end of the sight tube is 4 inches from the mirror, the angles subtended at the eye by the field are 15 and 20 degrees for the minor and major axes, respectively. The mirror when placed as shown in figure 2 serves as a baffle to prevent any light from screen S_2 falling on the test surface.

2. MECHANICAL DETAILS

The mechanical details may, of course, be varied to suit the maker's materials and choice. The photometer used at the Bureau employs the box, track, lamp housing, and scale of a Sharp-Millar [10] photometer. The photometric cube and eyepiece were removed and the diaphragm-diffusing-screen arrangement described in the previous section installed. Since this type of photometer is no longer commercially available a description of the mechanical details will serve as a guide for anyone wishing to construct one.

The box (fig. 2) is about 4 by 4 by 22 inches. The lamp, *L*, is moved by means of an endless cord which passes over a drum, *Dr*, which is turned by the handwheel, *H*. The sight tube may be turned in its collar to view the test surface at various angles. In order to avoid errors due to light reflected from the interior of the box a series of baffles, *B*, made of fiber is placed between the lamp and the screen S_1, and the interior is painted with a flat (mat) black paint. These baffles are carried on two light rods and are attached to each other and the lamp housing by cords. When the lamp moves toward S_1 the housing pushes the baffles successively in front of it and when it moves away from S_1 the cords pull the baffles one after another into their original position. The lamp housing carries an index, *I*, the shadow of which falls upon the translucent scale in the side of the box and thus there is no parallax. The scale is covered by red plastic to preserve the dark adaptation of the photometric observer. This arrangement also makes it unnecessary to provide a light for reading the scale, which is a great convenience, and avoids the usual scale marked on a space-wasting rod protruding from the box. Since readings are taken in a dark room, no stray light will enter the photometer through the translucent scale. It would be necessary to provide a shutter to cover the translucent scale if readings were taken in a lighted room, the shutter being opened only to read the scale after a setting had been taken.

[10] Elec. World **51**, 181 (1908); Elec. Rev. (New York) **52**, 141 (1908); Electrician (London) **60**, 562 (1907-08).

The lamp housing has a second index on the side opposite the scale index to facilitate the accurate positioning of the filament of the lamp at the unity mark of the photometric scale. The housing runs on a track made of angle brass fastened to the sides of the box. The single wheel has a spring to force it against the track to prevent sidewise motion.

IV. SUMMARY

A photometer, such as described in this paper, makes possible the determination of scotopic and mesopic luminance, such as that of fluorescent and phosphorescent materials. The use of a comparison field of color temperature 2,360° K and the mechanical control of the luminance of the comparison field are in accord with current American opinion on the datum and method of evaluating luminances in the mesopic and scotopic regions. Luminance so evaluated takes the Purkinje effect into account and correlates perfectly with brightness subjectively evaluated.

The photometer has been used for nearly 3 years in routine measurements of the luminance-time (brightness decay) curve of phosphorescent materials, as well as to determine both the luminance and chromaticity of the fluorescent light from papers impregnated or coated with fluorescent chemicals. In measuring the luminance of phosphorescent materials, different observers agree within about 5 percent in the region near 10 effective microlamberts, but the spread between observers increases to about 25 percent when the luminance is in the region of 0.005 effective microlambert. The measurement of fluorescent materials has not been extensive. However, some measure of the effect of color is given by tests of blue fluorescence at about 100 effective microlamberts where 4 observers made observations within a little less than 25 percent and tests of yellow fluorescence where with the same observers the results did not spread by as much as 10 percent at about 200 effective microlamberts. The use for determining chromaticity (where the spectral composition of the comparison source must remain constant while the luminance is varied) has been so satisfactory at low luminances that a photometer has been designed with a much wider range of luminance than the present photometer possesses. This increased range will be adequate for measuring the chromaticity of nonluminescent materials in the photopic range of luminance.

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FREEZING TEMPERATURE OF BENZOIC ACID AS A FIXED POINT IN THERMOMETRY

By Frank W. Schwab and Edward Wichers

ABSTRACT

The freezing temperature of benzoic acid is found to be reproducible with a precision comparable to that of the ice point and somewhat superior to that of the steam point as usually observed in standardizing laboratories. For use in the calibration of thermometric instruments the acid is contained in a partially evacuated glass cell provided with a thermometer well. When thus confined, and if not heated excessively, the substance maintains a constant composition for long periods of time. When properly manipulated, the acid in a given cell exhibits a freezing temperature reproducible from day to day within 1 millidegree.

The triple point of pure benzoic acid is 122.362° ±0.002° C. Under a pressure of 1 atmosphere of dry air the freezing temperature is 0.013 degree higher. Corresponding elevations for oxygen and nitrogen are 0.001 and 0.015 degree, respectively. The pressure coefficient of the freezing temperature is 0.039 degree/atm. The change in volume of the acid on freezing is −0.138 cm³/g. The corresponding calculated value for the density of the solid at the freezing temperature is 1.27 g/cm³. The solubility of oxygen in the liquid at its freezing temperature, under a pressure of 1 atm., is 0.132 g/1,000 g of acid; that of nitrogen is 0.073 g.

An appendix deals with a method of calculating temperatures, in the ranges −190° to 0° C and 0° to 660° C, from observations with a platinum thermometer. For this purpose power-series equations are used instead of the Callendar and Callendar-Van Dusen equations. Tables are included to facilitate the computation of temperature.

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I. INTRODUCTION

Temperatures in the range 0° to 660° C, on the International Temperature Scale, are defined in terms of platinum resistance thermometers, of specified characteristics, by means of the equation

$$R_t = R_0 (1 + At + Bt^2).$$

R_0 is the resistance at the temperature of equilibrium between ice and air-saturated water at normal atmospheric pressure, and A and B are constants determined by calibration at the temperatures of condensing water vapor and sulfur vapor, respectively, each under a pressure of 1 atm. The temperature of melting ice is relatively insensitive to variations of atmospheric pressure (0.0076 degree C/atm.), but the accuracy of calibration at the steam and sulfur points is limited by the accuracy which can be attained in making barometric measurements. The boiling temperature of water changes by 0.001 degree C with a change in pressure of 0.027 mm of mercury. Since barometric pressure measurements commonly are not made to an accuracy greater than about 0.1 mm of mercury in standardizing laboratories, the accuracy of calibration of platinum thermometers is limited to 0.003 to 0.004 degree C, except in a very few laboratories that are equipped for fundamental work in thermometry. The sulfur point, used with the steam and ice points to determine the constant in the second-power term in the equation, need not be fixed as accurately as the steam point unless temperatures are measured near the sulfur point or in the range beyond it.

A readily reproducible fixed temperature in the vicinity of 100° C, insensitive to variations in barometric pressure, would be useful for the calibration of thermometers, even if it could not be reproduced more exactly than the steam point, because the calibration procedure would be greatly simplified if barometric measurements did not need to be made. The present paper deals with the use for this purpose of the freezing temperature of benzoic acid. The term "freezing temperature" is here used in preference to "freezing point" because, as will be explained later, it is proposed to establish arbitrary conditions of observation, which may cause the freezing temperature to be fixed anywhere between the triple point (122.362° C) and the freezing point (freezing temperature under 1 atm. of dry air, 122.375° C).

Experience with benzoic acid in another project [1] indicated that this substance possesses the properties required of a thermometric standard, of which the more important are as follows: (1) Availa-

[1] Frank W. Schwab and Edward Wichers, *Preparation of benzoic acid of high purity*, J. Research NBS 25, 747 (1940) RP1351.

bility in an adequate degree of purity; (2) sufficiently large latent heat at the change of phase; (3) adequate velocity of crystallization; (4) existence in only one crystalline form at temperatures near the freezing point; and (5) stability under the conditions of use. Benzoic acid can be obtained commercially in a degree of purity better than 99.95 mole percent, and the purity can be increased to 99.998 mole percent or better by relatively simple laboratory procedures, most readily by a method of fractional freezing described in a previous paper.[2] The cryoscopic behavior of the substance is such that 0.001 mole percent of impurity dissolved in the liquid acid (but insoluble in the solid) depresses the freezing temperature 0.00075 degree C. Hence the attainable purity will permit reproducing the freezing temperature to within 0.001 to 0.002 degree C. The same amount of impurity causes the freezing temperature of the acid to change 0.00075 degree C between 0- and 50-percent frozen. As will be shown later, variations in the proportion frozen can be held within a small part of this range.

The heat of fusion of benzoic acid is reported to be about 140 j/g, or 150 j/ml, which is a little less than half that of water. Many observations made during earlier work show that the heat of fusion, combined with a high velocity of crystallization, is sufficient to maintain satisfactory thermal equilibrium between the solid and liquid when the system loses heat at any reasonably slow rate. During these observations no evidence was ever obtained of the transformation of the liquid to more than one crystalline form.

II. MATERIALS, APPARATUS, AND PROCEDURES

1. MATERIAL AND PROCEDURE FOR FILLING THE CELLS

The benzoic acid used for the experimental work reported in this paper was prepared by fractionally freezing a quantity of commercial benzoic acid as described by the authors in an earlier publication.[3] Measurements of the freezing range,[4] when the acid was freed of water in a manner which did not cause the formation of a significant amount of benzoic anhydride, indicated that the acid used to determine the reproducibility of the freezing temperature was 99.998 mole percent pure. That used to study some of the properties of the acid was of somewhat lower purity.

To avoid variations in freezing temperature which would have resulted from changes in the moisture content of air had the acid been frozen in open vessels, the acid was kept in sealed cells for all observations of the constancy and reproducibility of the freezing temperature. These cells, shown in figure 1, were cylindrical in shape, 5 cm in diameter, and about 25 cm long. A thermometer well 8 mm in diameter extended nearly the length of the cylinder, and an extension of the well about 12 cm long served as a handle. The capacity of each cell was about 425 ml.

[2] Frank W. Schwab and Edward Wichers, *Purification of substances by slow fractional freezing*, J. Research NBS 32, 253 (1944) RP1588.
[3] See footnote 2.
[4] Frank W. Schwab and Edward Wichers, Precise Measurement of the Freezing Range as a Means of Determining the Purity of a Substance, Temperature—Its Measurement and Control in Science and Industry, p. 256–264 (Reinhold Publishing Corporation, New York, N. Y., 1941).

Before the cell was sealed to the apparatus shown in figure 2, about 380 g of the acid (365 ml), carefully fused in a beaker or other suitable vessel and containing a small amount of water, was transferred to the cell through a side tube. The volume of liquid acid was adjusted so as to leave a free space of 50 to 60 ml in the cell. The acid was allowed to freeze completely and the cell was sealed in place as shown

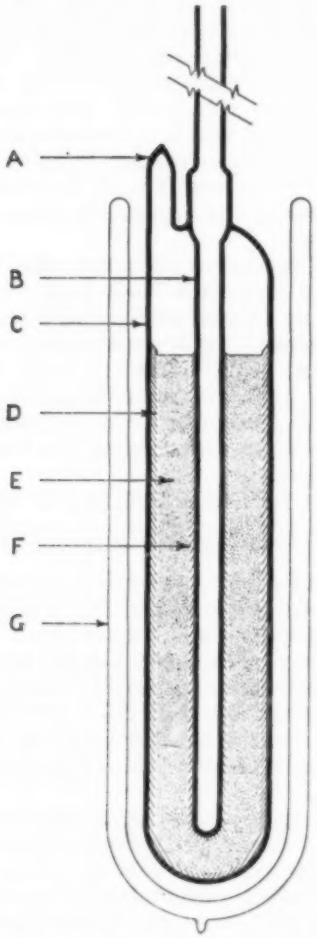

FIGURE 1.—*Benzoic acid fixed-point cell.*

A, Side-tube; *B*, thermometer well; *C*, cell proper; *D*, solid benzoic acid; *E*, mixture of crystals and liquid *F*, solid benzoic acid; *G*, Dewar flask.]

in figure 2, with the aeration-tube, *B*, completely withdrawn. The acid was melted again and tube *B* was inserted, through the sidearm extended, into the liquid and adjusted with its end near the bottom of the cell. The opening at *K* between *B* and the side arm extended was closed by forcing a short piece of rubber tubing over the outside tube and was finally sealed with pycene. With stopcock 9 open,

and stopcock 2 open to outlet 1, the liquid was saturated with air, which was dried over phosphorus pentoxide and free of carbon dioxide, forced under the necessary pressure into the system at *H*.

The next steps in the procedure were designed to remove the water which is always present when benzoic acid is fused in contact with ordinary air. Liquid benzoic acid saturated, at temperatures near its freezing point, with air having a partial pressure of 5 mm of water vapor, contains about 0.06 mole percent of dissolved water. This amount of water depresses the freezing temperature between 0.04 and 0.05 degree C. In addition to moisture gained from the air there was

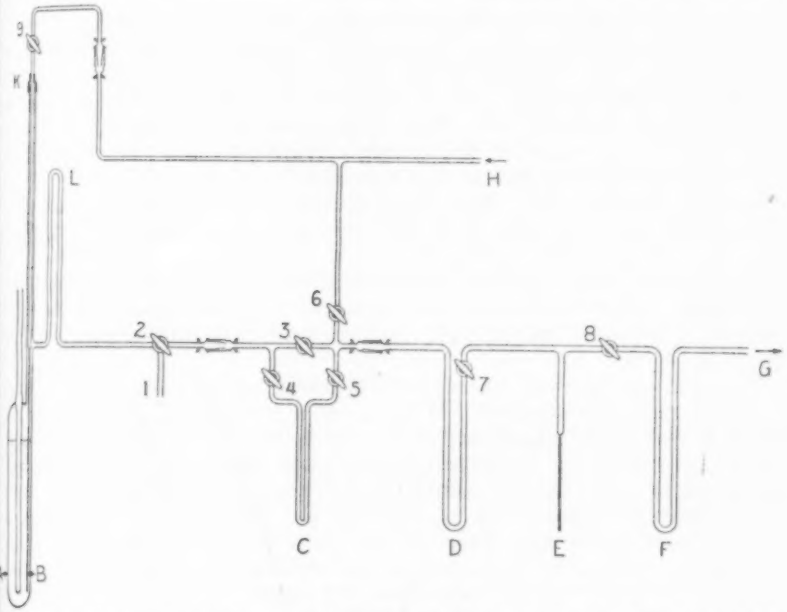

FIGURE 2.—*Apparatus for filling the benzoic acid fixed-point cell and for determining water in benzoic acid.*

A, Benzoic acid fixed-point cell; *B*, aeration-tube; *C*, manometer; *D*, trap of known volume; *E*, capillary trap; *F*, trap; *G*, vacuum connection; *H*, dry air source; *K*, rubber-tubing-connection sealed with pycene; *L*, air condenser for benzoic acid; 1, outlet for dry air; 2, 3, 4, etc. 2-mm stopcocks.

usually some that had been added intentionally to convert to benzoic acid small amounts of benzoic anhydride which might have been formed during the operations of purification. It was therefore necessary to dry the acid in the cells quite thoroughly to avoid excessive differences among the freezing temperatures in the several cells. This was done by pumping off the gases evolved while the acid slowly froze in the cell. The evolution of dissolved oxygen and nitrogen helped materially to sweep out the water vapor. The acid was allowed to freeze completely. To keep it from freezing so rapidly as to entrap much of the evolved gases, it was warmed at intervals with the soft flame of a hand torch. The acid was again fused and saturated with dry air. During this operation much of the acid that had sublimed while it was previously freezing and had condensed in the cell side of the inverted U-tube, *L*, melted and flowed back into the cell. The

acid was allowed to freeze a second time. This time the discharged gases were pumped off through stopcock 2, which was open to the manometer, *C*, and trap *D* with stopcock 6 closed. During the pumping the trap was cooled with liquid air. When the pumping was completed, the trap was isolated from the rest of the apparatus, by closing stopcocks 3 and 7, and allowed to warm to room temperature. The known volume of the trap and the pressure indicated by the manometer gave a measure of the amount of water removed from the acid. *E* is a capillary receiver not used in this work and *F* is a guard trap. This apparatus and its use are described in greater detail in another publication.[5]

The amount of water removed during the second freezing was in each case enough to indicate the need of fusing the acid a third time. After the acid was saturated this time with dry air, stopcock 9 was closed and the aerating tube withdrawn far enough to leave its tip opposite the *T* outlet to *L*. The opening at *K* was again sealed vacuum tight in the manner previously described, and water, together with the atmospheric gases, was pumped from the acid while it was allowed to freeze. Not more than 0.0036 g of water, equivalent to about 0.006 mole percent or 0.0009 percent by weight, was pumped from any of the cells during the third evacuation. Because of the relatively long time required for the acid to freeze, a small part of this water may have formed as the result of the conversion of acid to anhydride. This behavior will be discussed in a later section of the paper.

The acid was allowed to freeze completely under vacuum, and then to cool to room temperature. Dry air at a pressure of about 21 cm of mercury was then admitted, after which the side tube was sealed. Under this condition the pressure increased somewhat when the acid was fused because the increase in volume accompanying fusion more than offset the amount of air dissolved. When the acid began to freeze, the pressure was about 25 cm, or one-third of an atmosphere. Because the volume of free space in the cells was not the same in each case, this pressure varied somewhat, by amounts not exactly known, in the group of cells prepared for observations of the freezing temperature.

Several other cells, filled in the manner described, were used for observations on the stability of the acid. Still another cell (fig. 4), to be described later, was provided with a side arm assembly consisting of a stopcock and a ball-joint connection so that various gases could be admitted at known pressures for observations on the effect of pressure and of dissolved atmospheric gases. The triple point of the acid was also measured in this same apparatus.

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[5] Frank W. Schwab and Edward Wichers, *A physical method for determining residual water and other volatile materials in pure substances*, J. Research NBS **33**, 121 (1944) RP1600.

2. APPARATUS FOR MEASURING TEMPERATURES

The temperature measurements were made with platinum resistance thermometers of the coiled-filament type described by Meyers,[6] with a resistance at 0° C of about 25 ohms. The outside diameter of the thermometers was about 7 mm and the length of the coiled filament was 3 to 3.5 cm. The resistances were measured with a precision Mueller[7] bridge of the type G–2, No. 8069, made by the Leeds & Northrup Co. The apparatus was equipped with a switch that reversed the galvanometer current and thereby doubled the scale deflection caused by a given unbalance in the bridge. For convenience the bridge was connected to a four-place selector switch. The galvanometer had a sensitivity of 10 mm/microvolt, a period of not over 6 seconds, a critical external damping resistance of not less than 50 ohms and a coil resistance of 23.5 ohms. The optical arm of the galvanometer was 5.5 m long. With a reversing switch on the bridge, it provided a scale deflection of 32 mm for an unbalance of the bridge of 0.0001 ohm. It was thus readily possible to estimate changes in resistance to a few millionths of an ohm. All corrections were made to a millionth of an ohm in order to obtain an adequate measure of the reproducibility.

Before the series of measurements reported in this paper were made, the resistance bridge was calibrated by the Resistance Measurements Section of this Bureau. Two of the thermometers, 535 and 618, together with the bridge, were calibrated at the steam point to 0.0001 degree C by C. S. Cragoe and H. F. Stimson of the Heat Measurements Section, with a precision manometer by means of which the height of the mercury column was fixed with an accuracy within 1 micron. The sulfur point was determined in the regular way by the Thermometry Section, also of this Bureau. A much less accurate calibration was required at the sulfur point than at the steam point, since all of the temperatures measured were close to 122.4° C. At this temperature, errors arising from an error of calibration at the sulfur point are only about one-fiftieth of the error at the sulfur point itself. The bridge and each of the thermometers, 535 and 618, were calibrated in the same way after the measurements were completed, to disclose, if possible, any changes in the resistance-measuring equipment. The other thermometers, 515 and 587, were calibrated in the regular way by the Thermometry Section, before the measurements were begun. At the completion of the observations, theremometer 587 was also calibrated with the same accuracy as 535 and 618. The characteristics of the four thermometers, as determined by these calibrations, are given in table 1.

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[6] C. H. Meyers, *Coiled-filament resistance thermometers*, BS J. Research **9**, 807 (1932) RP508.
[7] E. F. Mueller, Precision Resistance Thermometry, Temperature—Its Measurement and Control In Science and Industry, p. 162 to 179 (Reinhold Publishing Corporation, New York, N. Y., 1941).

TABLE 1.—*Characteristics of thermometers*

Calibration by N B S—	Date calibrated	c[a]	δ[a]
THERMOMETER 535			
Thermometry Section	Nov. 17, 1938	0.0039243	1.491
Heat Measurements Section	July 30, 1941	.00392454	1.494
	Dec. 3 and 4, 1941	.00392453	1.494
	Jan. 22, 1942	.00392452	1.494
THERMOMETER 618			
Thermometry Section	Aug. 4, 1941	0.0039241	1.493
Heat Measurements Section	Dec. 3 and 4, 1941	.00392409	1.492
	Jan. 22, 1942	.00392409	1.492
THERMOMETER 587[b]			
Thermometry Section	Sept. 27, 1940	0.0039244	1.494
	July 30, 1941	.00392438	1.492
Heat Measurements Section	Dec. 3 and 4, 1941	.00392441	1.494
	Jan. 22, 1942	.00392438	1.492
THERMOMETER 515			
Thermometry Section	Mar. 15, 1938	0.0039226	1.499
Heat Measurements Section	(c)	(c)	(c)

[a] c is the fundamental coefficient of the resistance coil of the thermometer and may be expressed as

$$\frac{R_{100}-R_0}{100R_0},$$

in which R_{100} and R_0 are the resistances of the coil at 100° and 0° C, respectively. δ is also a constant which is characteristic of the individual thermometer. It is determined by calibration at the ice, steam and sulfur points. Both constants are for the Callendar equation, which is given in the appendix to this paper.

The values for c and δ given in line 1 under each thermometer were determined in the regular way by the Thermometry Section of the National Bureau of Standards. The values given for δ in lines 2 and 3, under thermometer 618 and in lines 2, 3, and 4, under thermometers 535 and 587, were not determined but were computed from the new values of c, reported by the Heat Measurements Section and from the values of δ given in line 1.

[b] The constants reported for Sept. 27, 1940, and July 30, 1941, were obtained before the thermometer was broken; the other constants were obtained after it was repaired.

[c] No calibration.

3. PROCEDURES FOR MEASURING TEMPERATURES

(a) AT THE BENZOIC ACID POINT

The procedure usually followed in observing the freezing temperatures in the cells was as follows: The cell was heated in an electric oven kept several degrees above the freezing point of the acid, usually at about 130° C. When the acid was completely fused and had reached the temperature of the oven, the cell was removed and rather vigorously shaken so that the acid cooled uniformly. More rapid cooling at one point was caused by placing a cap of wet paper on the end of the side-tube (A in fig. 1). This caused a small amount of acid to crystallize and thus prevented excessive undercooling of the bulk of the liquid. If the crystals were not present, the acid sometimes undercooled as much as 15 degrees C, and the amount of solid suddenly formed was excessive. Normally, as the cell cooled, a mush of fine needle-like crystals appeared quite suddenly throughout the liquid. Although only a small fraction of the acid was frozen, the crystals were so well interlaced that they did not tend to settle out on subsequent standing. The cell was then rolled up in a piece of soft cloth

and placed in a close-fitting Dewar flask. The open end of the Dewar flask was packed with cotton to provide further insulation. Before the cell was put into it, the Dewar flask was warmed approximately to the freezing point of the acid by placing in it for 15 to 20 minutes a companion cell also containing freezing benzoic acid. This was done to prevent the rapid freezing of acid in the cell to be measured, which otherwise would have been caused by the loss of a considerable amount of heat to the cold flask. When the cell which was to be observed was in place in the Dewar flask, the resistance thermometer was inserted in the thermometer well. After about 10 minutes, measurements of resistance were begun. They were continued at least until the resistance reached its maximum (usually within 30 minutes) and nearly always for a considerably longer period. In a number of instances two sets of resistance measurements were made, one in which the thermometer current was 1.00 ma; the other, 1.41 ma. With the latter current the power input was twice that of the former. The difference in resistance between the two sets of measurements, when subtracted from the resistance observed with a current of 1 ma, provided the correction necessary to give resistances corresponding to zero thermometer current.

Usually, observations were made on several cells in close sequence by connecting the several thermometers to the bridge in rotation by means of the selector switch.

Temperatures corresponding to observed resistances were computed by the method described in the appendix to this paper. For observations of small differences in temperature, with a given thermometer, it was not always necessary to compute actual temperatures. For these relative measurements it was often sufficient to observe changes in the interval between the ice point and the benzoic acid point, since the change of resistance as a function of temperature in the vicinity of the benzoic acid point was accurately known. The approximate coefficient was 0.0001 ohm/millidegree.

(b) AT THE ICE POINT

The fundamental calibrations of the measuring instruments were made before and after the series of observations that gave the precision of the benzoic acid fixed-point cell. In addition, observations at the benzoic acid point were bracketed between observations at the ice point, made the same day, in order to disclose and, if possible, to correct for any variation in the resistance-measuring equipment. Two benzoic acid points and three ice points were usually measured with a thermometer during a day.

Measurements at the ice point were made as follows:[8] Shaved ice obtained from clear cakes was washed with distilled water. The mush was thoroughly mixed in an open porcelain enamel pan to approach saturation with air, and then transferred to a precooled Dewar flask. The coil of the thermometer was immersed 20 to 25 cm, the mush was pressed lightly around the thermometer and measurements

[8] The "ice point," or temperature of equilibrium between ice and air-saturated water at normal atmospheric pressure, has been a basic fixed point in nearly all measurements of temperature. It was reported in the Technical News Bulletin of the National Bureau of Standards, No. 305, p. 71 (1942), that for work of the highest precision it is desirable to avoid the small variations in the ice point resulting from contact of the melting ice with the atmosphere. For this purpose the triple point of water has advantages. A direct comparison between the ice point and the triple point for the same sample of water shows a difference of 0.00997 degree C.

of the resistances were recorded when they became constant. As with the measurements at the benzoic acid point, observations were made with thermometer currents of 1.00 and 1.41 ma, to permit extrapolation to zero current. A correction for impurities in the ice was obtained from conductivity measurements of the ice water at the time of calibration and on other occasions when it was desirable to report temperatures to the highest accuracy. Clear ice was of high purity and the correction was usually not more than 0.00001 to 0.00002 ohm.

In table 5 are given the resistances of thermometers 587, 535, 618, and 515 as measured at the ice points during the time most of the measurements reported in this paper were made. These measurements show the maximum variation observed during a period of about 1 month.

III. STABILITY OF BENZOIC ACID

In the course of this work, benzoic acid was not found to undergo any measurable irreversible decomposition when heated at temperatures below 150° C. Evidence of this will be presented later. However, the acid does undergo a reversible decomposition to benzoic anhydride and water. Since this reaction must be controlled if the acid is not to suffer a variable or progressive change in purity, and hence in freezing temperature, extensive observations concerning it were made. Some of these observations have been reported in an earlier publication.[9] When the acid is enclosed in a sealed container the water produced simultaneously with the anhydride cannot escape, and the reaction therefore can proceed only until an equilibrium is reached. At the outset it was thought that the acid would have to be brought to some state of equilibrium with the products of its own dissociation if reproducible freezing temperatures were to be obtained. Accordingly, four cells were kept above freezing temperature except during the short periods when observations of the freezing temperature were being made, until they reached equilibrium, as evidenced by constancy of the freezing temperature. This was done by keeping the cells in an electrically heated oven, in which mechanical circulation of air kept the temperature constant within 1 degree. The temperature of the oven was intended to be about 10 degrees C above the freezing temperature of the acid. An actual measurement made after the observations were begun showed the temperature of the oven to be 131.6° C. The observed freezing temperatures of the cells are given in table 2. It will be noted that 10 days or longer were required for the acid to reach equilibrium with benzoic anhydride and water. The slight variability in the observed temperatures over longer periods, up to 8 weeks, is attributable to a lack of reproducibility caused by the presence of about 0.015 mole percent each of dissolved anhydride and water. The small differences in the total depressions observed in the several cells were probably caused by differences in the initial content of water or of anhydride resulting from uncontrolled variations in the drying of the acid when the cells were filled.

[9] Frank W. Schwab and Edward Wichers, *Preparation of benzoic acid of high purity*, J. Research NBS 24, 747 (1940) RP 1351.

TABLE 2.—*Stability of benzoic acid at 131.6° C* [a]

Cell 11		Cell 12		Cell 13		Cell 14	
Time at 131.6° C	T_f	Time at 131.6° C	T_f	Time at 131.6° C	T_f	Time at 131.6° C	T_f
hr	° *C*	*hr*	° *C*	*hr*	° *C*	*hr*	° *C*
0	122.3577	0	122.3558	0	122.3565	0	122.3598
21	122.351	123	122.344	---	---	20	122.356
38	122.347	161	122.343	432	122.343	58	122.346
105	122.341	265	122.342	560	122.342	97	122.343
124	122.340	301	122.342	671	122.338	223	122.339
143	122.341	383	122.342	693	122.338	558	122.338
161	122.340	419	122.339	730	122.339	964	122.337
180	122.341	530	122.341	---	---	1,075	122.337
247	122.338	548	122.336	---	---	---	---
265	122.339	566	122.338	---	---	---	---
284	122.339	602	122.340	---	---	---	---
302	122.339	671	122.338	---	---	---	---
337	122.340	707	122.338	---	---	---	---
405	122.339	726	122.338	---	---	---	---
422	122.339	1,073	122.336	---	---	---	---
525	122.337	1,325	122.337	---	---	---	---
579	122.339	1,391	122.337	---	---	---	---
682	122.338	---	---	---	---	---	---
977	122.337	---	---	---	---	---	---
995	122.337	---	---	---	---	---	---
1,061	122.337	---	---	---	---	---	---
1,281	122.336	---	---	---	---	---	---
1,300	122.337	---	---	---	---	---	---
1,318	122.338	---	---	---	---	---	---
1,361	122.337	---	---	---	---	---	---
After reversion.	122.3573	After reversion.	122.3549	After reversion.	122.3578	After reversion.	122.3600

[a] In column 1 under each cell is given the total time in hours that the cell was kept at 131.6° C. Proper allowance was made for each time the acid was frozen. The temperature of freezing (T_f°C) represents the maximum temperature observed.

A few observations of the equilibrium established at 150° C showed that at this temperature the final concentrations of anhydride and water are approximately double those at 131.6° C.

The last temperature recorded for each cell in table 2, designated "after reversion," indicates the freezing temperature after the completion of the other observations and after the original condition of the acid had been restored. It will be noted that in the long periods during which the cells were kept at 131.6° C, no measurable irreversible decrease in the purity of the acid occurred. The average deviation of the freezing temperatures at the end of the several periods from those at the beginning was 0.7 millidegree.

Further evidence of the absence of thermal decomposition was given by the behavior of one cell that was kept at 131.6° C for nearly a year. The total depression of the freezing temperature observed during this interval was 5 millidegrees. Since the thermometer used to measure the freezing temperature at the beginning of the period was subsequently found to be variable by more than 5 millidegrees, the change that may have occurred is not precisely known, but it obviously was not large. The same cell was later kept at 150° C for nearly a month. After the first few days required to establish the anhydride equilibrium, there was no further depression of the freezing temperature, which would have occurred had there been a measurable amount of thermal decomposition or of a chemical reaction with the glass of the containing vessel. From these results it may be concluded that benzoic acid is adequately stable for use in thermometry, provided it is not heated for long periods at temperatures much above

150° C, and provided account is taken of the reversible formation of benzoic anhydride and water.

During the observations made while the cells were kept at 131.6° C, it was noted that the freezing temperature tended to rise if the acid was kept near freezing for longer than the usual short periods required for measurements. If all the acid in a cell was allowed to freeze slowly and then remelted for a short time, there was a marked rise in the freezing temperature. When this was repeated several times, the freezing temperature returned to that of acid containing no anhydride, as shown in table 2. Obviously the acid in the cells was reverting to its original condition. This came about for two reasons. From the fact that the equilibrium concentrations of anhydride and water at 150° C were markedly greater than those at 131.6° C, it follows that the equilibrium concentrations near the freezing temperature (122.4° C) must be lower than those at 131.6° C. This alone is probably not enough to account for complete reversion to benzoic acid, although observations made at the freezing temperature indicate that the equilibrium concentrations of water and anhydride are lower than 0.003 mole percent each at this temperature. The probable explanation of complete reversion of the anhydride and water during slow freezing is as follows: As the acid freezes the anhydride and water remain almost completely in solution in the liquid phase. As freezing progresses, their concentrations in the liquid phase progressively increase. If the eutectic temperature of the system is as much as 10 degrees C below the freezing point of the acid, the initially minute concentration of the two "impurities" may be multiplied some thousands of times before the liquid phase completely disappears. This huge change in concentration causes the rate of recombination to increase enormously. It is doubtless true that the anhydride and water do not remain ideally in the liquid phase as freezing progresses, but this condition must be rather closely approached at the slow rate of freezing which occurs if the cell is kept in the Dewar flask.

From the data in table 2 it can be estimated that the initial rate of formation of anhydride and water at 131.6° C is not great enough to cause in 1 hour a lowering of the freezing temperature by as much as 1 millidegree. When a cell is prepared for an observation it takes only a short time, at most half an hour, to heat the acid, once it is completely fused, to a temperature a few degrees above its freezing point. As the rate of formation of the anhydride during the melting period, which is considerably longer, must be much lower than at 131.6° C, it may be concluded that the total amount of anhydride and water formed while the cell is being prepared for an observation is not enough to depress the freezing temperature by as much as 1 millidegree. Since even the minute amounts that are formed tend to revert to acid during the subsequent freezing, it is apparent that cells kept at room temperature during the periods between observations would not be unreliable because of the dissociation reaction. Because of the absence of appreciable amounts of anhydride and water as "impurities" in such cells, the observed freezing temperatures would also be more sharply reproducible than in cells maintained above the freezing temperature during the intervals between observations. Accordingly, all subsequent observations of the reproducibility of the freezing tempera-

ture were made on cells kept at room temperature when not in use. In occasional exceptions, for example, when the formation of crystals was faulty, the period required to reheat the cell was very short.[10]

IV. REPRODUCIBILITY OF THE FREEZING TEMPERATURE

After the acid in each of the five cells had been restored to the condition existing before the series of observations in which the cells were kept at 131.6° C, a large number of observations were made to determine the reproducibility of the freezing temperature.[11] Most of these observations were made during a period of 1 month. Four thermometers were used. Two of the thermometers, 535 and 618, were calibrated at the steam point with the high degree of accuracy previously mentioned. This made it possible to assign absolute values to the observed temperatures, although the emphasis in this series of observations was on the constancy and reproducibility of the temperature of a particular cell as measured with a particular thermometer. It should be noted that the observed temperatures have no significance either as the triple point of benzoic acid or as its freezing temperature under 1 atm of dry air, because the conditions in the cells were intermediate between these two defined conditions. The pressure in the cells was about one-third of an atmosphere, but there was some variation in the pressure from cell to cell, and also in the purity of the acid in the several cells, resulting from the way in which the cells were filled.

Figure 3 [12] illustrates the course of measurements of a particular cell. The lower curve represents observations made with a thermometer current of 1.00 ma and the upper one with 1.41 ma. The average difference between the two sets of measurements, when subtracted from those represented by the lower curve, would give an extrapolated curve of resistances with zero thermometer current.[13]

In table 3 are given six sets of data, all for one cell, but obtained with three thermometers, similar to those used in figure 3 but extrapolated to zero thermometer current.

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[10] In connection with this discussion, it may be pointed out that the direction and magnitude of the shift in the equilibrium between the acid anhydride and water in the interval between 150° C and the freezing point suggest that no measurable amounts of anhydride and water are likely to exist under equilibrium conditions at room temperature.

[11] Thanks are expressed to J. L. Clark, of this Bureau, for his help during these observations.

[12] The observations in figure 3 were made by the Heat Measurements Section.

[13] In accordance with a paper by Mueller (see footnote 7), it has been customary to assume that, in the range from 0° to 500° C, the temperature rise produced by a constant thermometer current is independent of the temperature and the medium in which the thermometer is placed. This is true only when the environments of the thermometer do not differ materially with respect to loss of heat at the temperatures being measured. In cases where there is doubt as to whether the heating is the same at all temperatures or in different media at one temperature, the observed resistances may be corrected to those corresponding to zero thermometer current by making observations with two different thermometer currents. For example, the environment of the thermometer in the measurements at the ice point reported in this paper, was shaved ice in water. At the benzoic acid point the thermometer, inserted in the well B of the cell (fig. 1) was separated from the freezing mixture of benzoic acid by the Pyrex thermometer well and a thin air space. Subtracting the difference between the resistances observed when 1.41 and 1.00 ma were used, from the resistance observed when 1.00 ma was used, gave the resistance for zero thermometer current. The difference between the resistances observed for each thermometer, 535, 618, 515 and 587, with thermometer currents of 1.41 and 1.00 ma, was 0.000209, 0.000184, 0.000167, and 0.000190 ohm at the benzoic acid point. The corresponding differences at the ice point were 0.000133, 0.000108, 0.000119, and 0.000120 ohms, respectively. The validity of these extrapolations is dependent on the assumption that the heat input and the temperature rise of the thermometers varies as the square of the current, which was verified by making measurements with thermometer currents of $\sqrt{0.50}$, 1.00, $\sqrt{2.00}$, and 2.00 ma. It is interesting to note that if the temperature at the benzoic acid point had been calculated from the resistances observed with 1.00 ma as the thermometer current, the benzoic acid point would have been in error by at least 0.5 millidegree (thermometer 515) and not more than 0.8 millidegree (thermometer 618). With a thermometer current of 2 ma, the error would have been 2.0 and 3.2 millidegrees, and larger for higher thermometer currents.

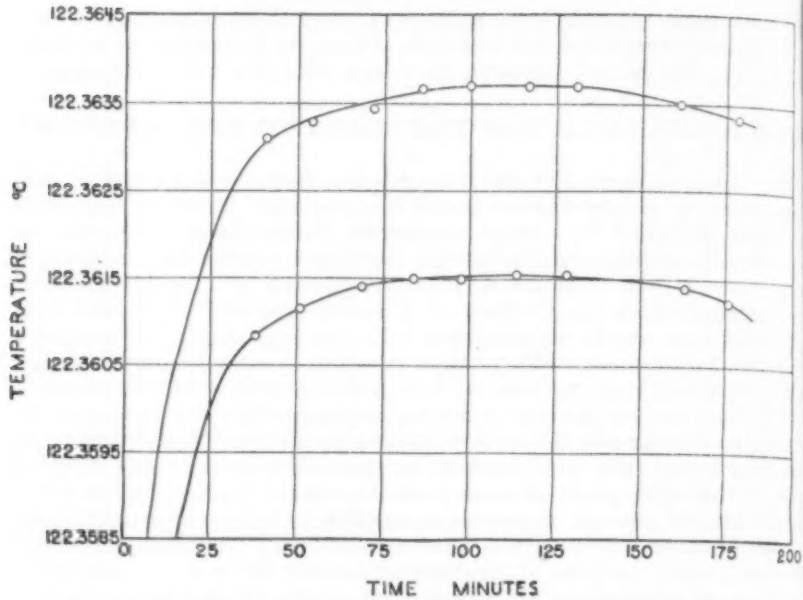


FIGURE 3.—*Constancy of temperature in a benzoic acid fixed-point cell.*

Lower curve, Thermometer current 1.00 ma; upper curve, thermometer current 1.41 ma.

TABLE 3.—*Constancy of temperature in a benzoic acid fixed-point cell*

[Cell 15]

Thermometer 587			Thermometer 535			Thermometer 618		
Date	Time	Temperature	Date	Time	Temperature	Date	Time	Temperature
	min	°C		*min*	°C		*min*	°C
	10	122.3577		12	122.3602		12	122.3608
	22	122.3596		24	122.3618		24	122.3621
	34	122.3600		36	122.3622		36	122.3622
	46	122.3601		48	122.3624		48	122.3624
Aug. 15, 1941	58	122.3601	Aug. 11, 1941	60	122.3625	Aug. 13, 1941	60	122.3624
	82	122.3600		72	122.3624		84	122.3624
	94	122.3599		84	122.3627		96	122.3624
	108	122.3599		120	122.3629		108	122.3625
	118	122.3599		132	122.3628		156	122.3628
	178	122.3599		180	122.3626			
				11	122.3605		11	122.3616
				23	122.3622		23	122.3633
				35	122.3626	Aug. 22, 1941	35	122.3637
				47	122.3627		47	122.3638
			Aug. 12, 1941	59	122.3628		107	122.3636
				83	122.3630			
				95	122.3630		6	122.3625
				119	122.3630		7	122.3627
							8	122.3628
							9	122.3629
						*Sept. 29, 1941	15	122.3630
							25	122.3633
							38	122.3636
							105	122.3636
							148	122.3633

* The thermometer was warmed to a temperature near the freezing temperature and then quickly placed in the cell.

TABLE 4.—*Precision of benzoic acid fixed-point cells*

Cell 11			Cell 12			Cell 13			Cell 14			Cell 15		
Date	Maximum temperature	Variation 60 to 120 minutes	Date	Maximum temperature	Variation 60 to 120 minutes	Date	Maximum temperature	Variation 60 to 120 minutes	Date	Maximum temperature	Variation 60 to 120 minutes	Date	Maximum temperature	Variation 60 to 120 minutes
THERMOMETER 535														
	°C	°C		°C	°C		°C	°C		°C	°C		°C	°C
Aug. 22, 1941	122.3598	0.0005	Aug. 20, 1941	122.3594	0.0007	Aug. 13, 1941	122.3616	0.0001	Aug. 20, 1941	122.3635	0.0001	Aug. 11, 1941	122.3629	0.0004
Aug. 26, 1941	122.3604	.0005	Aug. 21, 1941	122.3592	.0003	Aug. 22, 1941	122.3611	.0005	Aug. 21, 1941	122.3635	.0005	Aug. 12, 1941	122.3630	.0002
Aug. 27, 1941	122.3608	.0007	Aug. 25, 1941	122.3593	.0005	Aug. 26, 1941	122.3611	.0003	Aug. 27, 1941	122.3635	.0002	Aug. 25, 1941	122.3637	.0006
Sept. 13, 1941	122.3608	.0002	Sept. 3, 1941	122.3592	.0003	Sept. 2, 1941	122.3606	.0003	Aug. 29, 1941	122.3632	.0003	Aug. 28, 1941	122.3633	.0001
Average	122.3604$_5$	0.0004$_8$	Average	122.3592$_8$	0.0004$_8$	Average	122.3611$_0$	0.0003$_0$	Average	122.3634$_0$	0.0002$_8$	Average	122.3632$_5$	0.0003$_3$
Average deviation	0.0003$_5$	0.0001$_4$	Average deviation	0.0000$_3$	0.0001$_3$	Average deviation	0.0002$_5$	0.0001$_0$	Average deviation	0.0001$_2$	0.0001$_2$	Average deviation	0.0002$_8$	0.0001$_8$
Dec. 9, 1941	[a] 122.3609		Dec. 9, 1941	[a] 122.3595		Dec. 10, 1941	[a] 122.3612					Dec. 10, 1941	[a] 122.3631	
THERMOMETER 618														
Aug. 28, 1941	122.3609	0.0002	Aug. 26, 1941	122.3589	0.0007	Aug. 20, 1941	122.3615	0.0003	Aug. 12, 1941	122.3637	0.0008	Aug. 13, 1941	122.3635	0.0001
Sept. 2, 1941	122.3611	.0003	Aug. 27, 1941	122.3600	.0007	Aug. 21, 1941	122.3617	.0001	Aug. 25, 1941	122.3634	.0005	Aug. 22, 1941	122.3638	.0002
Sept. 3, 1941	122.3610	.0001	Aug. 29, 1941	122.3594	.0003	Aug. 27, 1941	122.3618	.0005	Sept. 2, 1941	122.3627	.0003	Aug. 26, 1941	122.3636	.0000
Sept. 17, 1941	122.3612	.0001	Sept. 12, 1941	122.3593	.0001	Aug. 28, 1941	122.3611	.0001	Sept. 12, 1941	122.3634	.0000	Aug. 29, 1941	122.3634	.0002
Average	122.3610$_5$	0.0001$_8$	Average	122.3594$_0$	0.0004$_5$	Average	122.3615$_7$	0.0002$_5$	Average	122.3633$_0$	0.0004$_0$	Average	122.3635$_8$	0.0001$_3$
Average deviation	0.0001$_8$	0.0000$_8$	Average deviation	0.0003$_0$	0.0002$_5$	Average deviation	0.0002$_0$	0.0001$_5$	Average deviation	0.0003$_0$	0.0002$_5$	Average deviation	0.0001$_3$	0.0000$_8$
Sept. 25, 1941	[a] 122.3613											Oct. 29, 1941	[a] 122.3636	
Oct. 2, 1941	[a] 122.3609											Dec. 16, 1941	[a] 122.3630	
THERMOMETER 515														
Aug. 29, 1941	122.3611	0.0004	Aug. 28, 1941	122.3601	0.0007	Aug. 29, 1941	122.3617	0.0007	Aug. 28, 1941	122.3640	0.0001	Aug. 27, 1941	122.3644	0.0004
Sept. 12, 1941	122.3617	.0001	Sept. 2, 1941	122.3610	.0002	Sept. 13, 1941	122.3633	.0004	Sept. 9, 1941	122.3638	.0000	Sept. 2, 1941	122.3637	.0002
Average	122.3614$_0$	0.0002$_5$	Average	122.3605$_5$	0.0004$_3$	Average	122.3625$_0$	0.0005$_3$	Average	122.3639$_0$	0.0000$_3$	Average	122.3640$_5$	0.0003$_0$
Average deviation	0.0003$_0$	0.0001$_5$	Average deviation	0.0004$_3$	0.0002$_2$	Average deviation	0.0008$_0$	0.0001$_5$	Average deviation	0.0001$_0$	0.0000$_3$	Average deviation	0.0003$_5$	0.0001$_0$
												Sept. 12, 1941	[a] 122.3644	
THERMOMETER [illegible]														
Aug. 20, 1941	122.3572	0.0001	Aug. 22, 1941	122.3549	0.0005	Aug. 11, 1941	122.3577	0.0000	Aug. 13, 1941	122.3599	0.0000	Aug. 15, 1941	122.3601	0.0002
Aug. 21, 1941	122.3571	.0001				Aug. 12, 1941	122.3576	.0002	Aug. 22, 1941	122.3600	.0004	Aug. 18, 1941	122.3595	.0003
Aug. 25, 1941	122.3576	.0002				Aug. 25, 1941	122.3582	.0008				Aug. 20, 1941	122.3600	.0003
									Average	122.3599$_5$	0.0002$_0$	Aug. 21, 1941	122.3600	.0004
Average	122.3573$_0$	0.0001$_2$				Average	122.3578$_1$	0.0003$_2$	Average deviation	0.0000$_5$	0.0002$_0$	Average	122.3599$_0$	0.0003$_0$
Average deviation	0.0002$_0$	0.0000$_4$				Average deviation	0.0002$_4$	0.0003$_0$				Average deviation	0.0002$_0$	0.0000$_5$
												Dec. 18, 1941	[a] 122.3634	

[a] Values not included in the averages.

Cell 11					Cell 12				
Date	Ice point	Average ice point	Benzoic acid point	ΔR	Date	Ice point	Average ice point	Benzoic acid point	
THERMOMETER 535					**THERMOMETER 535**				
	Ohms	*Ohms*	*Ohms*	*Ohms*		*Ohms*	*Ohms*	*Ohms*	*O*
Aug. 22, 1941	25.483892 25.483891	25.483891	37.680482	12.196591	Aug. 20, 1941	25.483816 25.483878	25.483847	37.680377	12
Aug. 26, 1941	25.483779 25.483818	25.483799	37.680400	12.196601	Aug. 21, 1941	25.483864 25.483891	25.483878	37.680396	12
Aug. 27, 1941	25.483885 25.483902	25.483894	37.680581	12.196687	Aug. 25, 1941	25.483777 25.483675	25.483726	37.680191	12
Sept. 13, 1941	25.483935 25.483947	25.483941	37.680646	12.196705	Sept. 3, 1941	25.483889 25.483885	25.483887	37.680418	12
Average	25.483881	25.483881	37.680527	12.196646	Average	25.483835	25.483835	37.680346	12
Range	0.000168	0.000142	0.000246	0.000114	Range	0.000216	0.000161	0.000227	0
Average deviation.	0.000041	0.000036	0.000086	0.000050	Average deviation.	0.000059	0.000054	0.000077	0
THERMOMETER 618					**THERMOMETER 618**				
Aug. 28, 1941	25.578982 25.578998	25.578990	37.819871	12.240881	Aug. 26, 1941	25.578852 25.578863	25.578858	37.819487	12
Sept. 2, 1941	25.578957 25.578960	25.578959	37.819849	12.240890	Aug. 27, 1941	25.578888 25.578956	25.578922	37.819682	12
Sept. 3, 1941	25.578936 25.578883	25.578910	37.819765	12.240855	Aug. 29, 1941	25.578954 25.578962	25.578958	37.819675	12
Sept. 17, 1941	25.578947 25.578969	25.578958	37.819855	12.240897	Sept. 12, 1941	25.578974 25.578986	25.578980	37.819699	12
Average	25.578954	25.578954	37.819835	12.240881	Average	25.578929	25.578930	37.819636	12
Range	0.000115	0.000080	0.000105	0.000042	Range	0.000134	0.000122	0.000212	0
Average deviation.	0.000024	0.000022	0.000025	0.000013	Average deviation.	0.000046	0.000040	0.000074	0
THERMOMETER 515					**THERMOMETER 515**				
Aug. 29, 1941	25.483294 25.483265	25.483280	37.673587	12.190307	Aug. 28, 1941	25.483300 25.483332	25.483316	37.673537	12
Sept. 12, 1941	25.483326 25.483316	25.483321	37.673701	12.190380	Sept. 2, 1941	25.483259 25.483216	25.483238	37.673530	12
Average	25.483301	25.483301	37.673644	12.190344	Average	25.483277	25.483277	37.673534	12
Range	0.000061	0.000041	0.000114	0.000073	Range	0.000116	0.000078	0.000007	0
Average deviation.	0.000021	0.000021	0.000057	0.000036	Average deviation.	0.000039	0.000039	0.000004	0
THERMOMETER 587					**THERMOMETER 587**				
Aug. 20, 1941	25.567094 25.567147	25.567121	37.803281	12.236160	Aug. 22, 1941	25.567151 25.567148	25.567150	37.803100	12
Aug. 21, 1941	25.567147 25.567163	25.567155	37.803319	12.236164					
Aug. 25, 1941	25.567074 25.566988	25.567031	37.803160	12.236144					
Average	25.567102	25.567102	37.803253	12.236156					
Range	0.000175	0.000124	0.000159	0.000020					
Average deviation.	0.000050	0.000048	0.000062	0.000008					

TABLE 5.—*Measurements of the ice and benzoic acid points*

Benzoic acid point	ΔR	Cell 13 Date	Ice point	Average ice point	Benzoic acid point	ΔR	Date	Ice p
35		THERMOMETER 535						THI
Ohms	*Ohms*		*Ohms*	*Ohms*	*Ohms*	*Ohms*		*Oh*
37.680377	12.196530	Aug. 13, 1941	25.483897 25.483900	25.483899	37.680662	12.196763	Aug. 20, 1941	25.48 25.48
37.680396	12.196518	Aug. 22, 1941	25.483891 25.483856	25.483874	37.680581	12.196707	Aug. 21, 1941	25.48 25.48
37.680191	12.196465	Aug. 26, 1941	25.483818 25.483827	25.483823	37.680502	12.196679	Aug. 27, 1941	25.48 25.48
37.680418	12.196531	Sept. 2, 1941	25.483903 25.483891	25.483897	37.680570	12.196672	Sept. 29, 1941	25.48 25.48
37.680346	12.196511	Average	25.483873	25.483873	37.680579	12.196706	Average	25.48
0.000227	0.000066	Range	0.000085	0.000076	0.000160	0.000091	Range	0.00
0.000077	0.000023	Average deviation.	0.000029	0.000025	0.000043	0.000030	Average deviation.	0.00
618		THERMOMETER 618						THI
37.819487	12.240629	Aug. 20, 1941	25.578939 25.578947	25.578943	37.819862	12.240919	Aug. 12, 1941	25.57 25.57
37.819682	12.240760	Aug. 21, 1941	25.578953 25.578969	25.578961	37.819910	12.240949	Aug. 25, 1941	25.57 25.57
37.819675	12.240717	Aug. 27, 1941	25.578956 25.578960	25.578958	37.819912	12.240954	Sept. 2, 1941	25.57 25.57
37.819699	12.240719	Aug. 28, 1941	25.578998 25.578978	25.578988	37.819890	12.240902	Sept. 12, 1941	25.57 25.57
37.819636	12.240706	Average	25.578963	25.578963	37.819894	12.240931	Average	25.57
0.000212	0.000131	Range	0.000059	0.000045	0.000050	0.000052	Range	0.00
0.000074	0.000039	Average deviation.	0.000015	0.000013	0.000018	0.000021	Average deviation.	0.00
15		THERMOMETER 515						THE
37.673537	12.190221	Aug. 29, 1941	25.483265 25.483277	25.483271	37.673629	12.190358	Aug. 28, 1941	25.483 25.483
37.673530	12.190292	Sept. 13, 1941	25.483235 25.483243	25.483239	37.673739	12.190500	Sept. 9, 1941	25.483 25.483
37.673534	12.190257	Average	25.483255	25.483256	37.673684	12.190429	Average	25.483
0.000007	0.000071	Range	0.000042	0.000032	0.000110	0.000142	Range	0.000
0.000004	0.000036	Average deviation.	0.000016	0.000016	0.000055	0.000071	Average deviation.	0.000
57		THERMOMETER 587						THE
37.803100	12.235950	Aug. 11, 1941	25.567147 25.567151	25.567149	37.803374	12.236225	Aug. 13, 1941	25.567 25.567
		Aug. 12, 1941	25.567095 25.567134	25.567115	37.803311	12.236196	Aug. 22, 1941	25.567 25.567
		Aug. 25, 1941	25.567005 25.567091	25.567048	37.803274	12.236226	Average	25.567
		Average	25.567104	25.567104	37.803320	12.236216	Range	0.000
		Range	0.000146	0.000101	0.000100	0.000030	Average deviation.	0.000
		Average deviation.	0.000040	0.000037	0.000035	0.000013		

Cell 14				Cell 15				
oint	Average ice point	Benzoic acid point	ΔR	Date	Ice point	Average ice point	Benzoic acid point	ΔR
ERMOMETER 535				THERMOMETER 535				
ns	*Ohms*	*Ohms*	*Ohms*		*Ohms*	*Ohms*	*Ohms*	*Ohms*
3878 3892	25. 483885	37. 680828	12. 196943	Aug. 11, 1941	25. 483890 25. 483860	25. 483875	37. 680761	12. 196886
3891 3899	25. 483895	37. 680845	12. 196950	Aug. 12, 1941	25. 483834 25. 483867	25. 483851	37. 680735	12. 196884
3902 3891	25. 483897	37. 680848	12. 196951	Aug. 25, 1941	25. 483675 25. 483825	25. 483750	37. 680657	12. 196907
3919 3892	25. 483906	37. 680833	12. 196927	Aug. 28, 1941	25. 483937 25. 483930	25. 483934	37. 680889	12. 196955
3896	25. 483896	37. 680839	12. 196943	Average	25. 483852	25. 483852	37. 680761	12. 196908
0041	0. 000021	0. 000020	0. 000024	Range	0. 000262	0. 000184	0. 000232	0. 000071
0009	0. 000006	0. 000008	0. 000008	Average deviation.	0. 000056	0. 000052	0. 000040	0. 000020
ERMOMETER 618				THERMOMETER 618				
3870 3914	25. 578892	37. 820009	12. 241117	Aug. 13, 1941	25. 579018 25. 579015	25. 579017	37. 820166	12. 241149
3808 3907	25. 578858	37. 819922	12. 241064	Aug. 22, 1941	25. 578954 25. 578911	25. 578933	37. 820070	12. 241137
3960 3965	25. 578963	37. 820009	12. 241046	Aug. 26, 1941	25. 578863 25. 578894	25. 578879	37. 819979	12. 241100
3986 3982	25. 578984	37. 820110	12. 241126	Aug. 29, 1941	25. 578962 25. 579023	25. 578993	37. 820122	12. 241129
3924	25. 578924	37. 820012	12. 241088	Average	25. 578956	25. 578955	37. 820084	12. 241129
0178	0. 000126	0. 000188	0. 000080	Range	0. 000160	0. 000138	0. 000187	0. 000049
0050	0. 000049	0. 000049	0. 000033	Average deviation.	0. 000050	0. 000050	0. 000060	0. 000014
RMOMETER 515				THERMOMETER 515				
3332 3292	25. 483312	37. 673911	12. 190599	Aug. 27, 1941	25. 483278 25. 483298	25. 483288	37. 673923	12. 190635
3260 3267	25. 483264	37. 673825	12. 190561	Sept. 2, 1941	25. 483261 25. 483279	25. 483270	37. 673825	12. 190555
3288	25. 483288	37. 673868	12. 190580	Average	25. 483279	25. 483279	37. 673874	12. 190595
0072	0. 000048	0. 000086	0. 000038	Range	0. 000037	0. 000018	0. 000098	0. 000080
0024	0. 000024	0. 000043	0. 000019	Average deviation.	0. 000010	0. 000009	0. 000049	0. 000040
RMOMETER 587				THERMOMETER 587				
3168 3192	25. 567180	37. 803630	12. 236450	Aug. 15, 1941	25. 567135 25. 567132	25. 567134	37. 803587	12. 236434
3148 3131	25. 567140	37. 803578	12. 236438	Aug. 18, 1941	25. 567147 25. 567191	25. 567169	37. 803572	12. 236403
3160	25. 567160	37. 803604	12. 236444	Aug. 20, 1941	25. 567121 25. 567175	25. 567148	37. 803594	12. 236446
0061	0. 000040	0. 000052	0. 000012	Aug. 21, 1941	25. 567163 25. 567191	25. 567177	37. 803642	12. 236465
0320	0. 000020	0. 000025	0. 000006	Average	25. 567157	25. 567157	37. 803599	12. 236437
				Range	0. 000070	0. 000043	0. 000070	0. 000062
				Average deviation.	0. 000024	0. 000016	0. 000025	0. 000019

In table 4 are recorded the systematic observations of five cells with the four thermometers. In addition to the date of each measurement, there are given the maximum observed temperature and the variation during the time interval 60 to 120 minutes. Also given are the averages of each set of measurements with a particular cell and thermometer and the average deviation of these measurements. Following these averages are single measurements of each of four cells with thermometer 535, and measurements of one cell (15) with each of the four thermometers, all made about 3 months after the others. At that time (Dec. 18, 1941, table 4) thermometer 587 had also been calibrated at the steam point with the same accuracy as 535 and 618, hence the measurements made with the three thermometers are directly comparable.

For a few days toward the end of the period during which the systematic observations were made the humidity became so high that it had a significant effect on the behavior of the bridge and galvanometer. This was apparent from erratic observations of the ice point. Only those measurements that were unmistakably unreliable from this cause have been excluded from table 4.

1. RELATIVE REPRODUCIBILITY OF THE ICE POINT AND THE BENZOIC ACID POINT

In table 5 the resistances observed at the ice point and at the benzoic acid point have been listed to show the relative reproducibilities of these two fixed points. The average of the average deviations of the difference of resistances between the ice and benzoic acid points is 0.000025_7 ohm. The greatest difference between any two observations of the resistance, in a set of observations with one thermometer, was 0.000262 ohm at the ice point (cell 15, thermometer 535) and 0.000246 ohm at the benzoic acid point (cell 11, thermometer 535).

The average of the average deviations obtained from the respective averages of each set of observations is 0.000032_8 ohm at the ice point and 0.000043_9 ohm at the benzoic acid point. These two averages are in about the same ratio to each other as that of the respective total resistances, 25 to 37 ohms. This suggests that the main source of variability in the observations, both of the ice point and of the benzoic acid point, may have been in the bridge. If this was true, both fixed points were reproduced with about equal precision, and possibly with a greater actual precision than is shown by the recorded resistances.

2. COMPARISON OF THERMOMETERS

In table 6 the average maximum temperatures observed in each cell with each thermometer have been combined to show the differences between observations of a particular cell with all possible pairs of the four thermometers. It will be seen that the differences between thermometers 535 and 618 are the smallest. As previously noted, these thermometers had received the specially accurate calibration at the steam point. The other two were calibrated in accordance with the routine practice of the Thermometry Section. In view of the reproducibility of the freezing temperature of each cell, as shown by table 4, it may reasonably be concluded that the comparisons of all other

pairs of thermometers reflect uncertainties in the calibration o resistance thermometers as normally practiced. In view of th known reproducibility of the ice point, nearly all of the uncertainty must result from observations of the steam point. Assuming no erro in calibration at the ice point, the interpolated error at the steam point is four-fifths the error at the benzoic acid point. These uncer tainties are no larger than can be expected from the errors o barometric measurements. The largest difference, that betwee thermometers 515 and 587, corresponds to a difference of 0.09 mm in the respective barometric readings.

TABLE 6.—*Comparison of thermometers* [a]

Cell	$T_{515}-T_{587}$	$T_{518}-T_{587}$	$T_{518}-T_{535}$	$T_{515}-T_{587}$	$T_{515}-T_{535}$	$T_{515}-T_{518}$
	°C	°C	°C	°C	°C	°C
11	0.0031$_5$	0.0037$_5$	0.0006$_9$	0.0041$_0$	0.0009$_5$	0.000
12	.0043$_8$	.0045$_9$	.0001$_2$	.0056$_8$	.0012$_7$	.001
13	.0032$_7$	.0036$_9$	.0004$_2$	.0046$_7$	.0014$_0$	.000
14	.0034$_5$	.0033$_3$	.0001$_0$	.0039$_8$	.0005$_0$	.000
15	.0033$_3$	.0036$_8$	.0003$_2$	.0041$_8$	.0008$_0$	.000
Average	0.0035$_2$	0.0037$_0$	0.0002$_7$	0.0045$_9$	0.0009$_8$	0.000
Average deviation	0.0003$_4$	0.0002$_8$	0.0002$_1$	0.0005$_9$	0.0003$_5$	0.000

[a] T is the average maximum temperature of a set of observations as given under each of the cells in tab 4. The subscripts to T define the thermometers with which the measurements were made.

3. COMPARISON OF CELLS

In table 7 the data of table 4 are combined so as to show the di ferences between the maximum temperatures of all possible pairs o cells as measured with each of the four thermometers. The greate difference between any pair (cells 12 and 15) is 4.2 millidegrees, an the smallest (between cells 14 and 15) is 0.05 millidegree. As pre viously noted, these differences are to be attributed partly to di ferences in the amount of benzoic anhydride or of water containe in the acid as the result of variations in the conditions under whic the cells were filled. The differences may also result in part fro differences in pressure of atmospheric gases in the cells when freezin begins. Although the pressures were nearly the same in all of th cells when they were sealed at room temperature, the pressures di fered at the freezing point because the volume of free space (vap space) was not closely controlled and the expansion which occurre as the cells were heated to the freezing temperature of the acid cause relative differences in the volumes of the free space. These diffe ences between the freezing temperatures in different cells can u doubtedly be made smaller by more careful control of the indicate factors. The freezing temperatures can also be brought very clo to a defined temperature, most readily to the triple point, by prop attention to the factors of purity and of pressure existing within t cell when freezing begins.

TABLE 7.—*Comparison of cells* [a]

Thermometer	$T_{12}-T_{11}$	$T_{13}-T_{11}$	$T_{14}-T_{11}$	$T_{15}-T_{11}$	$T_{13}-T_{12}$	$T_{14}-T_{12}$	$T_{15}-T_{12}$	$T_{14}-T_{13}$	$T_{15}-T_{13}$	$T_{15}-T_{14}$
	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C
	-0.0011_7	0.0006_6	0.0029_3	0.0028_9	0.0018_2	0.0041_2	0.0039_7	0.0023_9	0.0021_5	-0.0001_5
	$-.0016_9$	$.0004_7$	$.0022_3$	$.0025_7$	$.0021_2$	$.0039_9$	$.0041_8$	$.0017_8$	$.0020_6$	$.0002_8$
	$-.0008_5$	$.0011_9$	$.0025_0$	$.0026_4$	$.0019_3$	$.0033_5$	$.0035_0$	$.0014_6$	$.0015_8$	$.0001_4$
	$-.0024_0$	$.0005_3$	$.0026_5$	$.0026_0$	.....	.....	.....	$.0021_2$	$.0020_7$	$-.0000_5$
Average	-0.0012_2	0.0006_9	0.0025_7	0.0026_5	0.0019_6	0.0037_9	0.0038_8	0.0019_9	0.0019_6	0.0002_3
Average Deviation.	0.0002_8	0.0002_1	0.0002_1	0.0000_8	0.0001_6	0.0002_9	0.0002_8	0.0003_1	0.0002_6	0.0001_2

[a] T is the average maximum temperature of a set of observations as given under each of the thermometers in table 4. The subscripts to T define the cells with which the measurements were made.

In connection with the foregoing discussion, it may be of interest to examine more closely the behavior of a cell as illustrated by figure 3 and table 3. It will be noted that some 35 or 40 minutes elapse before the temperature becomes constant within a few tenths of a millidegree in the normal course of observations. The lag of the thermometer can not account for more than a fraction of this interval, possibly 10 minutes. The remainder of the lag is believed to have the following explanation. Although the solid and liquid phases are brought very close to equilibrium by shaking the cell as the crystals form, a slight departure from equilibrium near the wall of the thermometer well occurs when the thermometer is placed in the well. Loss of heat to the thermometer causes a thin film of solid to form on the wall. Unless the acid is ideally pure this separation of crystals from the now agitated liquid will lower the purity of the liquid in the region immediately adjacent to and in contact with this thin film of solid. By a process of diffusion, possibly aided by slow convection within the liquid, the composition of this liquid layer gradually approaches that of the bulk of the liquid. As this goes on, the freezing temperature rises until there is no further change in composition. A substantially constant temperature is then maintained for a while. This reasoning is supported by the observations made with thermometer 18 on Sept. 29, 1941 (see table 3), which were obtained under conditions different from normal. The thermometer was warmed at the freezing temperature in an auxiliary cell and then quickly transferred to cell 15. Under these conditions only a small quantity of acid froze around the thermometer well, with a correspondingly smaller change in concentration of impurity in the layer of liquid bounding this solid. It will be noted that in this instance the temperature rose to within a few tenths of a millidegree of the maximum in a much shorter time than usual.

Decline from the maximum temperature, as shown by the curves in figure 3, comes about from one or both of two causes. One is the increasing concentration of impurities in the liquid as freezing progresses from the outer wall of the cell toward the thermometer well. The other, and possibly the more significant one in this instance, is the lowering of pressure within the cell as freezing progresses. The contraction of the liquid on freezing is greater than the volume of atmospheric gases discharged by the liquid as it freezes. Hence there is a net decrease in pressure and, as will be shown in a later section of this paper, a lowering of the freezing temperature.

In cells to be prepared in the future it is proposed to use a much lower pressure of gas, so that the effects of a change of pressure during freezing will be minimized.[14]

V. FREEZING TEMPERATURES OF THE PURE ACID UNDER DEFINED CONDITIONS

In addition to the group of cells used for the study of the reproducibility of the freezing temperature, one cell was prepared for the measurement of the freezing temperature of the acid under known pressures of oxygen, nitrogen, and a mixture of these gases. The

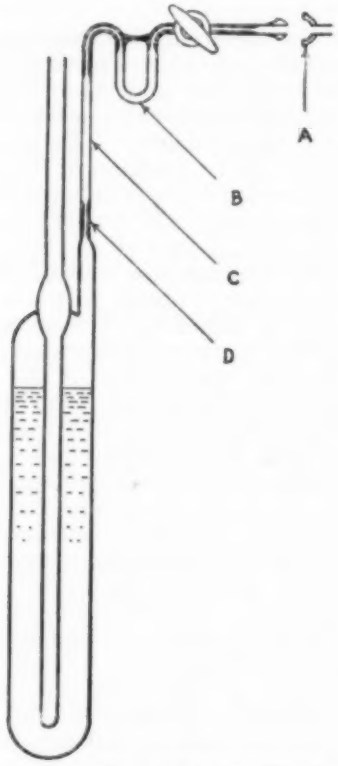


FIGURE 4.—*Cell used for observations of the freezing temperature under defined conditions.*

A, Movable ball-joint connection; *B*, trap; *C*, air condenser; *D*, capillary tube (2 mm).

triple point of the acid and the variation of the freezing temperature as a function of pressure were also measured in this cell. The cell shown in figure 4, differed from the others in that it could be attached to a source of variable pressure of selected gases. The capillary

[14] C. S. Cragoe and H. F. Stimson in unpublished observations at the triple point of water, made in a cell similar to that shown in figure 1, froze a thick layer of ice around the thermometer well and then, by warming the well, melted a thin layer next to it. This provided a surface at equilibrium temperature between ice and liquid water which had been purified by the process of freezing. This surface almost entirely surrounded the thermometer and hence controlled its temperature. This technic may prove advantageous with the benzoic acid cell but has not yet been tried. A similar technic was suggested by W. P. White, J. Am. Chem. Soc. **56**, 20 (1934).

portions of the connecting tube retarded the tendency for benzoic acid to sublime out of the cell when molten, and the larger portions served as condensers for the small amount of vapor that did pass the capillaries. The spherical joint, *A*, made it possible to rock the tube, if desired, while it was connected to the system for supplying gases and measuring the pressure.

When the acid in this cell was to be prepared for an observation, it was melted with a flame rather than in the oven. Care was taken to heat the acid slowly and uniformly so as to avoid overheating it. To get the desired mush of crystals in the liquid, the cell was manipulated in the manner previously described, with the additional detail that capillary *D* was kept cool, so that crystals of the acid would collect at this point and keep liquid from flowing into the trap or to the stopcock while the cell was being shaken. The cell was kept in a previously warmed Dewar flask during the temperature measurements. Further details of the manipulation required by special conditions of observation will be given in the appropriate paragraphs.

1. DETERMINATION OF THE TRIPLE POINT

To prepare for the determination of the triple point the acid was freed of water and atmospheric gases by evacuation of the cell while the acid was allowed to freeze slowly. The melting and freezing were repeated until no further change of pressure occurred when the cell was connected at *A* (fig. 4) to an evacuated system connected with a mercury manometer. Once the cell was freed of gases in the manner indicated, it did not require attachment to the gas-supply train during the observations of the triple point.

The triple point was measured on three consecutive days and twice more about a month later. The two later measurements were made between series of observations of the freezing temperatures under oxygen and nitrogen. They served as a check on the absence of any significant change in the composition of the acid which might have resulted from the repeated meltings.

The five observations of the triple point are given in table 8. It will be noted that the range of the five observations, including the two made after several measurements had been made under other conditions, is 0.9 millidegree, and that the changes during the series were not progressive. The small random variations possibly can be ascribed to differences in the fraction of acid frozen, that is, to the fact that observations were not made each time at exactly the same point in the freezing range of the slightly impure acid.

TABLE 8.—*Triple point of benzoic acid*

Date	Triple point
	°C
Sept. 23, 1941	122.361$_8$
Sept. 24, 1941	122.362$_3$
Sept. 25, 1941	122.362$_1$
Oct. 21, 1941	122.361$_4$
Oct. 24, 1941	122.362$_3$
Average	122.362$_0$

The acid used for these measurements was known to cont a small amount of impurity. To make the necessary correcti of the triple point, the freezing temperature of the acid in this under 1 atm of dry air was compared with that of acid of known pur also under 1 atm of dry air and observed in another apparatus wh will be described in a later section. The freezing temperature of acid used for the triple-point measurements was 6 millidegrees bel that of the pure acid. The amount of impurity, confirmed by measurement of the freezing range, was found to be 0.0084 m percent, which corresponds to a lowering of the freezing temperature 6 millidegrees. This correction has been applied to the temperatu in table 8. By adding an uncertainty of 1 millidegree involved the triple-point measurements to the uncertainty of 1 millideg attached to the freezing temperature in dry air of the pure acid, value of the triple point of pure benzoic acid can be given as 122.3 ±0.002° C.

2. FREEZING TEMPERATURES UNDER DIFFERENT PRESSURES OXYGEN AND OF NITROGEN

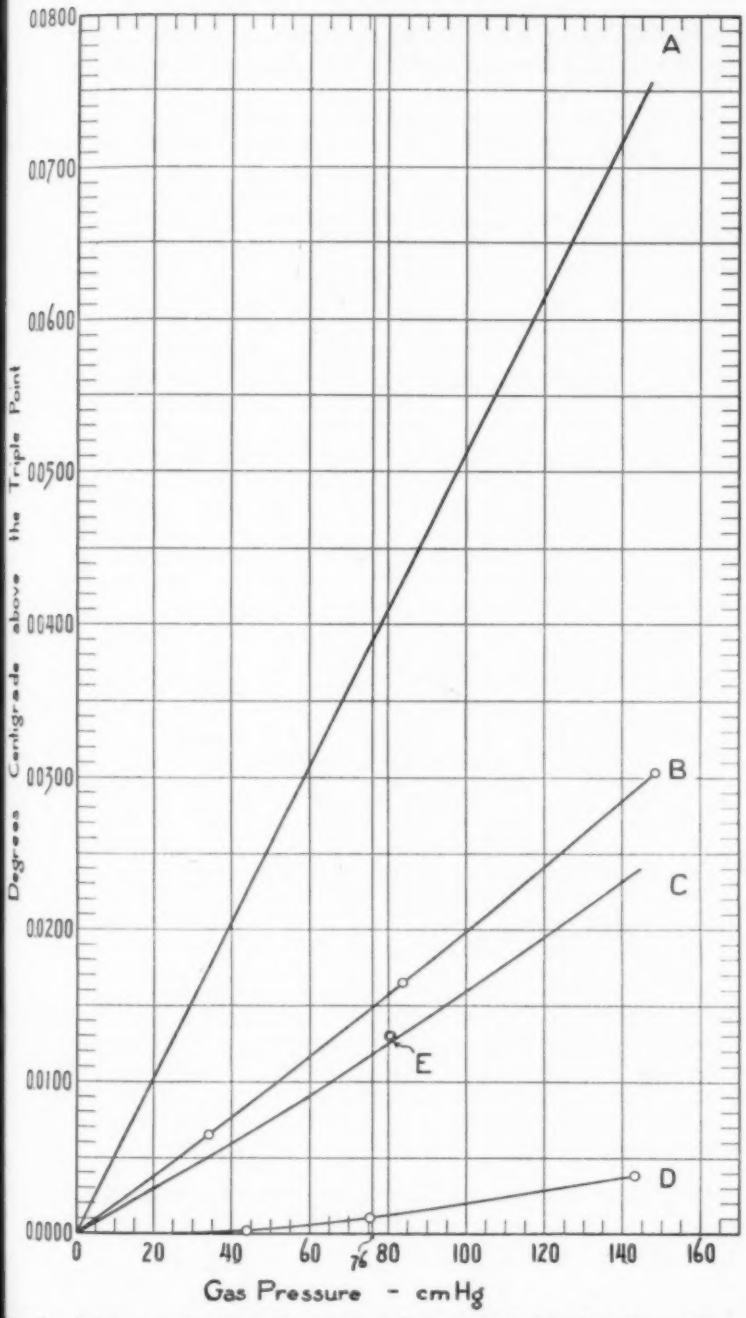
To measure the freezing temperatures in equilibrium with selec pressures of oxygen or nitrogen, the acid in the cell was first freed gases in the manner described in the preceding section. With acid in the cell at room temperature, gas was admitted at a selec pressure, which, after a few trials, bore a known relation to the press which would exist in the cell after it was isolated from the train the acid had been melted, shaken long enough to insure saturati with gas, brought to the standard conditions for observations of freezing temperature, placed in a Dewar flask, and then shaken minutes longer to insure equilibrium. When the freezing temperat reached its maximum value, the actual pressure in the cell was chec by setting the manometer to the predicted pressure and then open the stopcock. The change in the manometer never exceeded a f centimeters. The pressure in the cell was computed from the mano eter setting (predicted pressure), the observed pressure after the was opened to the manometer, and the known volumes of the space in the manometer and in the cell.[15]

The oxygen and nitrogen used for these measurements were, spectively, 99.87 and 99.74 percent pure, as determined from analy made by Martin Shepherd and Shuford Schuhmann of the Chemistry Section of this Bureau. Both gases contained so argon. Other impurities consisted primarily of oxygen in the nitrog and of nitrogen in the oxygen. The gases were dried over phospho pentoxide but not otherwise purified. Each gas was introduced i the cell in three successive steps, up to a maximum pressure of ab 2 atm. Between the two series of measurements, the triple po was redetermined to make sure that no change in the purity of acid had occurred. The results of the measurements are given the third column of table 9 and in curves B and D of figure 5.

[15] The ratios of the gas space of the system to the gas space of the cell v_s/v_c and of the gas space of the nometer to the gas space of the cell v_m/v_c were found to be 2.17 and 1.17, respectively. These ratios constant over the range of pressures measured. The pressure in the cell was computed from the re

$$p_c = 2.17P_s - 1.17p_m,$$

in which p_c = pressure in the cell, p_m = pressure in the manometer and P_s = pressure in the system, consists of the cell and the manometer.



URE 5.—*Difference between the triple point and the freezing temperature of enzoic acid in equilibrium with variable pressures of nitrogen, of oxygen, and of r, and the effect of pressure on the freezing temperature.*

ssure effect; B, equilibrium with nitrogen; C, equilibrium with air (21 percent of oxygen and 79 per- nitrogen), computed from the observed values for oxygen and for nitrogen; D, equilibrium with en; E observed freezing temperature of benzoic acid (122.375$_2$° C) in equilibrium with air under a ure of 80.1 cm of Hg (table 9).

recorded temperatures include the correction of 6 millidegrees impurities in the acid, as described in the section on the triple p

TABLE 9.—*Freezing temperature of benzoic acid in equilibrium with oxygen, nitr and air and the solubility of oxygen and of nitrogen in liquid benzoic acid freezing temperature*

Temperature (triple point 122.362$_0$° C)	Gas pressure [a]	Degrees above triple point	Δt (pressure effect) [b]	Δt (freezing point lowering)	Mole fraction $\times 10^{-5}$	g (1.00 benz acid)-
			NITROGEN			
°C	*cm* Hg	°C	°C	°C		
122.368$_8$	33.9	0.0065	0.0174	0.0109	14.5	0.03
122.378$_8$	83.4	.0165	.0427	.0262	34.9	.08
122.392$_3$	148.1	.0303	.0758	.0457	60.9	.13
			OXYGEN			
122.362$_2$	43.6	0.0002	0.0223	0.0221	29.5	0.07
122.363$_1$	75.0	.0011	.0384	.0373	49.7	.13
122.365$_8$	142.7	.0038	.0731	.0693	92.4	.24
			AIR CALCULATED FROM OXYGEN AND NITROGEN [c]			
122.365$_0$	20.0	0.0030	0.0102	0.0072	9.6	0.02
122.368$_1$	40.0	.0061	.0205	.0144	19.2	.04
122.371$_2$	60.0	.0092	.0307	.0215	28.7	.06
122.373$_8$	76.0	.0118	.0389	.0271	36.1	.08
122.374$_4$	80.0	.0124	.0410	.0286	38.1	.09
122.377$_6$	100.0	.0156	.0512	.0356	47.5	.12
122.380$_9$	120.0	.0189	.0614	.0425	56.7	.14
122.384$_3$	140.0	.0223	.0717	.0494	65.9	.15
			AIR-EQUILIBRIUM MEASURED			
122.375$_2$	80.1	0.0132	0.0410	0.0278	37.1	0.08
122.374$_5$	[d] 76.0	.0125	.0389	.0264	35.2	.08

[a] The values reported in this column are those for nitrogen, oxygen, and air, respectively, and were ob by subtracting the vapor pressure of benzoic acid at the triple point (4 mm of Hg) from the total p observed.

[b] These values were obtained by multiplying column 2 by the observed pressure coefficient, 5 degree C per centimeter Hg (table 10).

[c] All of the gases in air other than oxygen are included with nitrogen.

[d] Interpolated.

By interpolation from the data, the freezing temperatures of be acid under 1 atm of oxygen and of nitrogen are respectively 0.001 0.015_0 degree C above the triple point. The similar value fo calculated from these data (21 percent of oxygen and 79 perce nitrogen) is 0.012_0 degree C (see table 9). As will be noted later directly observed value for air was 0.012_5 degree C.

3. VARIATION IN THE FREEZING TEMPERATURE AS A FUNCT OF PRESSURE

In order to determine the solubility of oxygen and nitroge benzoic acid from the effect of varying pressures of these gases o freezing temperature, separate measurements of the effect of pre were necessary. These were made as follows: When certain o observations of freezing temperature in equilibrium with meas pressures of a gas were completed, the pressure of the gas in th was suddenly changed to some higher value. This produced an in

eous change in pressure but did not for some time alter the concentration of gas in the portion of the liquid around the thermometer ll, especially in the region near the thermometer coil. This lag in change of concentration of the gas was caused by the long path ough which gases dissolving at the upper surface of the liquid uld have to diffuse to reach the level of the thermometer coil. re was taken not to agitate the cell during these observations. The nge in temperature caused by the change in pressure usually was mplete within 3 minutes and always within 5. The change was shown be reversible by observations made when the sign of the pressure nge was reversed. The observed effects of these changes in pres- re are given in table 10. In the first column of table 10 is given pressure in centimeters before and after the pressure was suddenly nged. The pressure interval is given in column 2 and the corre- nding change in observed temperature in column 3. The changes freezing temperatures for a change in pressure of 1 cm and of 1 atm, calculated from the observed values, are given in columns 4 and 5, of table 10. The pressure coefficient is 0.038_9° C per atmosphere, shown in curve *A* of figure 5.

TABLE 10.—*Effect of pressure on the freezing temperature of benzoic acid*

Pressure	Change of pressure ΔP	ΔT	$\Delta T/\Delta P \times 10^{-4}$	Change of temperature per atmosphere
cm Hg	*cm* Hg	°*C*	°*C*/*cm* Hg	°*C*/*atm*
59.9	56.8	0.028_8	50.4	0.038_3
116.7	30.2	.015₆	51.5	.039₁
147.0	−86.8	−.044₈	+51.6	+.039₂
60.2				
Average			51.2	$.038_9$

SOLUBILITIES OF OXYGEN AND OF NITROGEN IN BENZOIC ACID

In column 4 of table 9 are given the interpolated values of the ct of pressure corresponding to the pressures at which the system observed in equilibrium with oxygen and nitrogen. By sub- cting the "elevation of the triple point" (column 3) caused by a en pressure of gas at equilibrium from the corresponding elevation sed by pressure as such (column 4), the depression of the freezing perature caused by the dissolved gas is obtained. These values given in column 5. The corresponding mole fractions of dissolved given in column 6 were calculated on the basis of the equation [16]

$$x=\frac{\Delta t L_{f_0}}{RT_{f_0}^2},$$

which x is the mole fraction of the solute; T_{f_0} is the freezing point the pure substance on the Kelvin scale; $\Delta t=T_{f_0}-T_f$, where T_f is initial freezing temperature (the temperature at which an

[16] Frank W. Schwab and Edward Wichers, Precise Measurement of the Freezing Range as a Means of Determining the Purity of a Substance, Temperature—Its Measurement and Control in Science and Industry, pp. 256–264 (Reinhold Publishing Corporation, New York, N. Y., 1941).

infinitely small quantity of solid is in equilibrium with the solution); L_{f_0} is the molal heat of fusion of the pure substance; and R is the gas constant. The solubility under a pressure of 1 atm, also shown in figure 6, is 0.132_1 and 0.073_2 g of oxygen and of nitgrogen, respectively, per thousand grams of acid. From figure 5 it will be seen that the solubility of each gas appears to increase slightly less than in direct proportion to its increase in pressure. It is believed that the measurements were made with sufficient accuracy to justify this conclusion. In view of the slight bearing of these observations on the principal

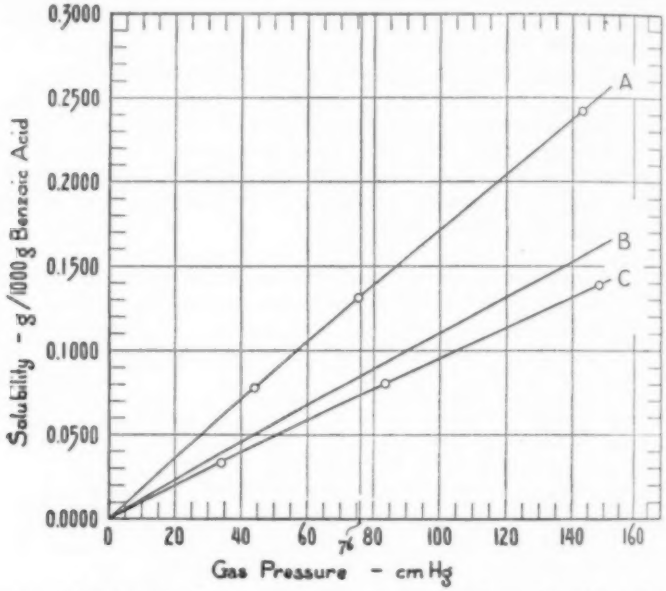


FIGURE 6.—*Solubility of oxygen, nitrogen, and air in benzoic acid at the freezing temperature.*

A, Solubility of oxygen, determined; B, solubility of air (21 percent oxygen and 79 percent nitrogen), computed from the determined solubility of oxygen and of nitrogen (table 9); C, solubility of nitrogen, determined.

object of this investigation, it did not appear justifiable to spend the time which would have been required to check the results by direct measurements of solubility.

5. FREEZING TEMPERATURE UNDER ONE ATMOSPHERE OF DRY AIR

The apparatus shown in figure 4 was used to determine the freezing temperature of the acid in equilibrium with air. The side arm of the cell was cut below D and a fritted-glass bubbler, which extended to the bottom of the cell, was inserted. It was attached with a ring seal arranged so that air could be forced into the liquid and out of the cell through a stopcock open to the atmosphere. Although liquid and solid acid were in the cell in about the same proportions as those existing during observations of the freezing temperature, dry air was passed through the cell long enough to insure a close approach to equilibrium

with dissolved oxygen and nitrogen under a combined pressure of 1 atm. The stopcock was then closed and the freezing temperature observed in the usual way. The freezing temperature was 122.375_2° C, and the simultaneously measured pressure in the cell was 80.5 cm of mercury (table 9 and fig. 5). During these observations the temperature of the upper end of the cell was probably slightly higher than it was while the air was being swept through the cell, hence the pressure rose slightly above 1 atm. The freezing temperature corrected to 1 atm was 122.374_5° C.

To determine the freezing temperature of benzoic acid in equilibrium with air in another manner, a different form of apparatus was used. This apparatus, which has been described in an earlier publication [17] is shown in figure 7. It was designed for measuring freezing ranges. The thermometer was centered in a cylindrical glass freezing tube 2 cm in diameter and about 25 cm long, provided with a glass jacket that could be evacuated if desired. The thermometer was supported by a ground-in glass head provided with an outlet tube for the passage of air from the freezing-range cell. The tip of the thermometer was about 2 cm from the bottom of the cell, and the depth of the liquid in the cell was 20 cm. Just above the bottom of the cell was a glass bubbler of the type described by Branham and Sperling [18] with orifices about 0.003 in. in diameter. The bubbler was provided with an inlet tube passing through the double-walled vessel and connected to a source of purified air dried over phosphorus pentoxide or conditioned to contain a desired partial pressure of water.

The freezing temperature of a portion of acid of high purity was measured as follows: While the acid was being melted in the apparatus it was stirred with air saturated with water at 0° C. It was then brought to a temperature about 10 degrees above the freezing temperature and thoroughly treated with air saturated with water at −25° C. Air saturated at this temperature contains a partial pressure of water vapor of about 0.5 mm of mercury, which is 10 times as much as is needed to cause virtually complete reversion of benzoic anhydride to benzoic acid.[19] The cell was then transferred to an oil bath that was kept 8 degrees below the freezing point of the acid. The acid undercooled about 0.5 degree C. When crystals suddenly formed, the temperature rose to within a few millidegrees of the equilibrium temperature in less than 2 minutes. About 5 percent of the acid was allowed to freeze, and then the temperature of the oil bath was quickly raised to the freezing temperature of the acid and kept constant within 0.01 degree C. This prevented further formation of solid and allowed the thermometer to indicate the temperature of equilibrium. The freezing temperature under these conditions was 122.369_9° C. Next, the acid was stirred with air dried over phosphorus pentoxide until the temperature rose to a constant value at 122.374_0° C, representing equilibrium in contact with dry air. This required 40 minutes, and observations were continued for 30 minutes longer. Thereafter the air used for stirring contained a partial pressure of water vapor of 4.6 mm of Hg, corre-

[17] Frank W. Schwab and Edward Wichers, Precise Measurement of the Freezing Range as a Means of Determining the Purity of a Substance, Temperature—Its Measurement and Control in Science and Industry, p. 256-264 (Reinhold Publishing Corporation, New York, N. Y., 1941).
[18] J. R. Branham and E. O. Sperling, *Bubbler tip of Pyrex glass for difficult absorptions*, J. Research NBS 22, 701 (1939) RP1214.
[19] Frank W. Schwab and Edward Wichers, *Preparation of benzoic acid of high purity*, J. Research NBS 25, 47 (1940) RP1351.

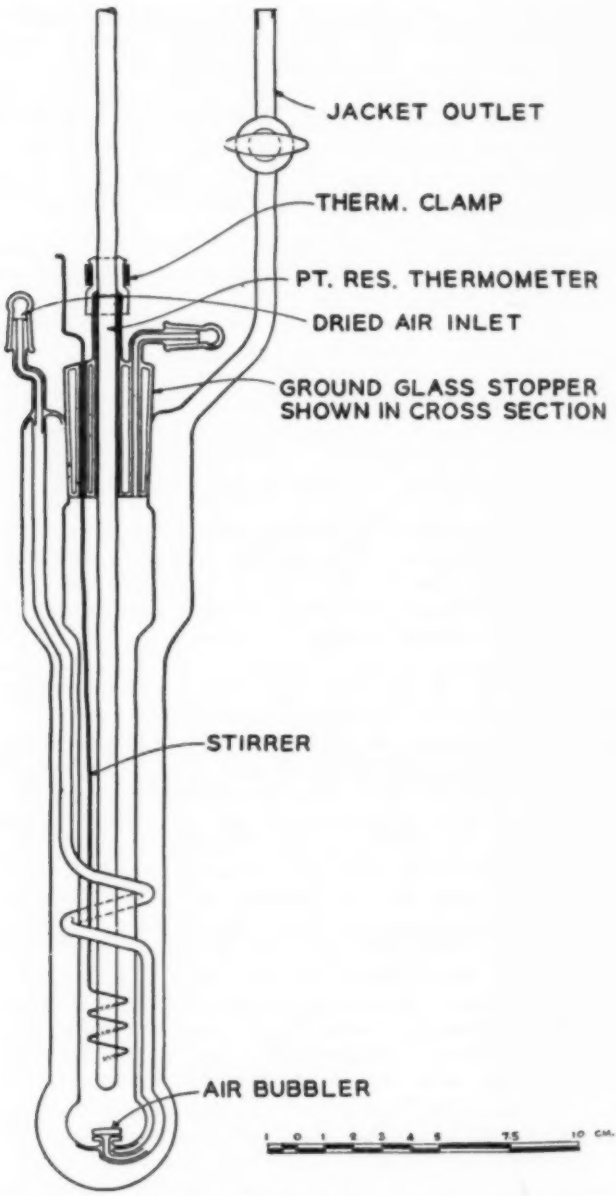


FIGURE 7.—*Apparatus for measuring the freezing temperature in equilibrium wi dry air and for determining the purity of the acid.*

sponding to saturation with water vapor at 0° C, whereupon the free ing temperature fell to 122.343$_5$° C. The two temperatures observe when the mixture of solid and liquid acid was in equilibrium wi air containing partial pressures of water vapor of 4.6 and 0.5 mm Hg, offered a means of extrapolating to the freezing temperature

uilibrium with dry air. The extrapolated temperature was 122.373° which agrees sufficiently well with the observed temperature der dry air to indicate that the acid, when thus observed, did not ntain a significant amount of benzoic anhydride.

After these observations were completed the purity of the acid was termined by measuring its freezing range in the same apparatus a procedure previously described.[20] Its purity was found to be .998$_4$ mole percent. The presence of 0.001$_6$ mole percent of impurity used an initial depression of the freezing temperature of 0.001$_2$ egree C, or of 0.001$_3$ degree C at the point in the freezing range hen 5 percent of the substance is frozen. This correction was there- re applied to the observed freezing temperature of the acid 22.374$_0$° C), giving a value for pure benzoic acid of 122.375$_3$° C, ith an estimated uncertainty of ±0.001 degree C.

I. CHANGE IN THE SPECIFIC VOLUME OF BENZOIC ACID THAT ACCOMPANIES FREEZING

The change in volume when benzoic acid freezes is of interest in nnection with its behavior in the sealed cells. No data were found he density of solid benzoic acid at or near its freezing point, and o apparently reliable values for the density of the liquid at that mperature. Observations by Timmermans and Burriel [21] on the quid at 130°, 155°, and 180° C permit extrapolation to the freezing mperature. The respective values for the density are 1.07494, 05218, and 1.02942 g/ml. Extrapolation to the freezing temper- ture gives 1.0819 g/ml. In this calculation the freezing temperature ven by Timmermans (122.45° C) was used so as to minimize the fect of possible systematic errors in the other temperatures.

There are no data for the density of the solid acid at temperatures gher than 23.3° C. The only available coefficient of expansion [22] for the interval between 15° and 30° C. This value is probably in ror because its calculation involved Lumsden's [23] determination of e density at 15° C (1.266 g/cm^3), a value which appears to be less curate than the one published by Hendricks and Jefferson [24] .3211±0.0001 g/cm^3 at 23.3° C). It was accordingly impossible make any reasonably good extrapolation to the density of the lid acid at its melting point. The change of volume on freezing as, therefore, calculated from the recorded value for the heat of sion per gram ΔH_f, 1,400 cc-atm, the observed pressure coefficient the freezing temperature $\Delta T/\Delta P$, 0.038$_9$° C/atm, and the freezing mperature of the acid T, 395.6° K, by means of the Clausius- lapeyron equation

$$\frac{\Delta P}{\Delta T}=\frac{\Delta H_f}{T(v_2-v_1)},$$

[20] Frank W. Schwab and Edward Wichers, Precise Measurement of the Freezing Range as a Means Determining the Purity of a Substance, Temperature—Its Measurement and Control in Science and dustry, p. 256-264 (Reinhold Publishing Corporation, New York, N. Y., 1941).

[21] Jean Timmermans and F. Burriel, Recherches sur les propriétés de quelques combinaisons organiques, udes à la temperature ordinaire, Chimie & Industrie, Special No., p. 196-7, March (1931).

[22] E. R. Smith, *The determination of the coefficient of cubical expansion of solid benzoic acid by means of a filled dilatometer*, BS J. Research **7**, 903 (1931) RP382.

[23] John Scott Lumsden, *The physical properties of heptoic, hexahydrobenzoic, and benzoic acids and their de- ivatives*, J. Chem. Soc. **87**, 90 (1905).

[24] S. B. Hendricks and M. E. Jefferson, *Anisotropy of molecular crystals. I. Experimental*, J. Optical c. of America **23**, 299 (1933).

in which v_1 is the specific volume of the liquid form, and v_2 that of the solid. The shrinkage which occurs on freezing, thus calculated, is 0.138 cm³/g. The corresponding calculated value for the density of the solid at the freezing temperature is 1.27 g/cm³.

The foregoing calculated value for the density at 122.37° C and the value of Hendricks and Jefferson for the density at 23.3° C give as the coefficient of cubical expansion, for the 99-degree interval, 0.00040 per degree.

Acknowledgment is made for the advice and many helpful suggestions received from members of the Heat Division, in particular E. F. Mueller, C. S. Cragoe, H. F. Stimson, and C. H. Meyers. Thanks are also expressed to C. L. Gordon for preparing the drawings.

VII. APPENDIX

Calculation of Temperatures in Platinum Resistance Thermometry

By Frank W. Schwab and E. R. Smith

The Callendar equation has been used for more than a half century for the computation of temperatures. During all these years there was little need for a departure from its use, but recently when it was appreciated that precision platinum resistance thermometers might be calibrated at temperatures other than the ice, steam, sulfur, and oxygen points, it became clear that a direct application of the fundamental equations offers advantages.

The fundamental equations can be modified in a regular manner to improve their application to the computation of temperatures. For the range from 0° to 660° C, one modification of the fundamental equation is described in this section. In the range from −190° to 0° C, two forms are given, of which the second is the more suitable for solution by the use of a slide rule.

1. RELATION BETWEEN THE POWER SERIES, CALLENDAR, AND CALLENDAR-VAN DUSEN EQUATIONS

The international scale of temperature between 0° and 660° C is defined by the resistance R_t of a platinum resistance thermometer by means of the formula

$$R_t = R_0(1 + At + Bt^2), \tag{1}$$

for which the constants, R_0, A, and B are determined from measurements of resistances at the melting point of ice, the boiling point of water, and the boiling point of sulfur. From −190° to 0° C, the temperature scale is obtained from the resistance by the formula

$$R_t = R_0[1 + At + Bt^2 + C(t-100)t^3], \tag{2}$$

in which the constants R_0, A, and B are the same as in formula 1 and the constant C is found from a measurement of resistance at the boiling point of oxygen.[25]

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[25] Compt. rend., Eighth General Conference of Weights and Measures, (Paris, 1933).

National Bureau of Standards certificates for platinum resistance thermometers report only values for the constants R_0, c, and δ for the Callendar formula

$$t=100\frac{R_t-R_0}{R_{100}-R_0}+\delta\left(\frac{t}{100}-1\right)\frac{t}{100},$$

in which the value to be used for $(R_{100}-R_0)$ is given by

$$(R_{100}-R_0)=100cR_0.$$

The value of the constant β may also be given for use in the Callendar-Van Dusen equation

$$t=100\frac{R_t-R_0}{R_{100}-R_0}+\delta\left(\frac{t}{100}-1\right)\frac{t}{100}+\beta\left(\frac{t}{100}-1\right)\left(\frac{t}{100}\right)^3 \qquad (3)$$

at temperatures below 0° C.

Equations 1 and 2 are the fundamental international equations. The constants for them can be computed from those of the equivalent forms of the Callendar and Callendar-Van Dusen equations. R_0, of course, remains the same for all. The relationships between the constants are readily obtained by writing the complete fundamental equation, 2, in the form

$$\frac{R_t}{R_0}=1+At+Bt^2+C(t-100)t^3 \qquad (4)$$

and the Callendar-Van Dusen equation in the equivalent form

$$\frac{R_t}{R_0}=1+c\left(1+\frac{\delta}{100}\right)t-\left(\frac{c\delta}{10^4}\right)t^2-\left(\frac{c\beta}{10^8}\right)(t-100)t^3. \qquad (5)$$

Since these equations are equivalent, comparison of coefficients gives

$$A=c\left(1+\frac{\delta}{100}\right),\ B=-\frac{c\delta}{10^4},\ C=\frac{-c\beta}{10^8}. \qquad (6)$$

The constants of the Callendar and Callendar-Van Dusen equations in terms of those of the fundamental equations are

$$c=A+100B,\ \delta=-\frac{10^4B}{c},\ \beta=-\frac{10^8C}{c}. \qquad (7)$$

4. INTERPOLATION OF TEMPERATURES BY USE OF THE POWER SERIES EQUATIONS

The power series equations can be expanded to make them more useful for the computation of temperatures by successive approximations. A simple graph together with a short table obviate more than one computation for a precision of the temperature within 0.001° C.[26]

[26] All of the precisions of the computation of temperature referred to in this appendix are dependent only on the method of computation. Other errors, such as errors of calibration, have been discussed by Brickwedde and Hoge, and others. Harold J. Hoge and Ferdinand G. Brickwedde, *Intercomparison of platinum resistance thermometers between −190° and 445° C*, J. Research NBS **28**, 217 (1942) RP1454.

(a) IN THE RANGE FROM 0° TO 660° C

With a calculating machine, the fundamental equations can b used as conveniently as the Callendar and Callendar-Van Dus equations to compute temperatures from resistances. For examp equation 1 can be written in the form

$$\left(\frac{R_t}{R_0}-1\right)=t(A+Bt) \text{ and } t=\frac{(R_t/R_0)-1}{A+Bt}.$$

If t_1 is a first estimation of the temperature,

$$t_2=\frac{(R_t/R_0)-1}{A+Bt_1},$$

etc.
When the measured temperature is between 0° and 100° C, and th first estimated temperature, t_1, is correct to within 1° C, one solutio of equation 9 yields the correct temperature to the nearest 0.01° C In the range between 100° and 660° C, two successive solutions a sufficient for this accuracy.

Better convergence can be obtained by the formula

$$t_2=\frac{[(R_t/R_0)-1]+Bt_1^2}{A+2Bt_1}$$

which can be derived from equation 1 by the Newton-Raphson metho of series approximation [27] or, less elegantly, by adding R_0Bt^2 to eac side of equation 1. With equation 10, if the first estimate of t temperature, t_1, is correct to within 2° C, the first solution of the equ tion for t_2 yields the temperature correctly to within 0.001° C over th complete range of validity of equation 1. The first estimation for can be made to within 2° C from a rough plot of R_t with respect to To make this plot, values of R_t for $t=0°$, 100°, 200° . . . 600° C can be quickly tabulated by little more than inspection of the funda mental formula $R_t=R_0(1+At+Bt^2)$. The results are plotted on scale such that 1 mm=1 degree and 0.1 ohm for a 25-ohm thermom eter. With sufficient accuracy the plot is taken as linear over eac 100-degree interval. Then only one computation with equation 10 needed to find the correct temperature to within the precision calibration of a platinum resistance thermometer.

(b) IN THE RANGE FROM −190° TO 0° C.

Equation 2 can be solved approximately to obtain

$$t_2=\frac{(R_t/R_0)-1}{A+Bt_1+C(t_1-100)t_1^2}$$

for temperatures below 0° C. For measurements with a 25-oh thermometer and with an initial estimate of the temperature mad correctly to within 1° C, the first temperature computed by equatio 11 differs from the correct temperature by 0.003° C at −25° C and b

[27] See also, Scarborough, Numerical Mathematical Analysis, p. 178, Johns Hopkins Press (1930).

.057° C at −190° C. The second computation, using the first as the stimated value, is correct to better than 0.001° C between 0° and -140° C and is in error by only 0.004° C at −190° C.

When equation 2 is treated by the Newton-Raphson method, there obtained

$$t_2=\frac{[(R_t/R_0)-1]+Bt_1^2+C(3t_1-200)t_1^3}{A+2Bt_1+C(4t_1-300)t_1^2}. \tag{12}$$

This equation appears unwieldly but is quite simple to use with the id of a modern calculating machine and will yield over the complete ange of 0° to −190° C temperatures correct to the nearest 0.001° C n the first computation when the initial estimate, t_1, is correct to ithin 2 degrees. If 0.005° to 0.01° C is sufficient precision, the initial stimate need be correct to within 5° C.

An equation of the same form as equation 12 but a little simpler in he final terms of the numerator and denominator can be found by dding Bt^2+nC$(t-100)t^3$ to each side of equation 2, written in the orm $(R_t/R_0)-1=At+Bt^2+C$(t$-100)t^3$. Then, on solving approxiately for t, there is obtained

$$t_2=\frac{[(R_t/R_0)-1]+Bt_1^2+nC(t_1-100)t_1^3}{A+2Bt_1+(n+1)C(t_1-100)t_1^2}. \tag{13}$$

By trial, it has been found that equation 13 gives as satisfactory convergence as equation 12 when n is assigned the value of 2.64, so that equation 13 becomes

$$t_2=\frac{[(R_t/R_0)-1]+Bt_1^2+E[(t_1/100)-1]t_1^3}{A+2Bt_1+F[(t_1/100)-1]t_1^2}, \tag{14}$$

in which $E=264$C and $F=364$C.

The following procedure is recommended for the calculation of temperatures by means of either equation 12 or 14.

3. PROCEDURE FOR THE CALCULATION OF TEMPERATURES BY USE OF THE POWER SERIES EQUATIONS]

Obtain the initial estimate of the temperature, correct to within 2° C from a very simple graph of R plotted with respect to t. This graph is made to a scale of 1 mm=1° C and 0.1 ohm. The point for $t=-190°$ is connected by a straight line to the point for $t=-100°$. The latter is connected by another straight line to the point for $t=0°$. The temperature corresponding to any resistance in the range covered can be read from the plot to within 2° C for use as t_1 with either equation 12 or 14. If equation 12 is to be used, values of the temperature functions useful for a quick computation are taken from table 11. If equation 14 is preferred, table 12 is used. In either case the following method is rapid.

TABLE 11.—*Data for computing temperatures in platinum resistance thermometry by the equations* [1]

$$t_2=\frac{[(R_t/R_0)-1]+Bt_1^2}{A+2Bt_1}$$

and

$$t_2=\frac{[(R_t/R_0)-1]+Bt_1^2+C(3t_1-200)t_1^2}{A+2Bt_1+C(4t_1-300)t_1^2}$$

in the ranges of temperature from 0° to 190° C and 0° to −190° C, respectively

—	$-\frac{t}{10^4}$	$-(t-300)\frac{t^3}{10^{12}}$	$\frac{t^2}{10^7}$	$(2t-200)\frac{t^2}{10^{10}}$
0	0. 000000	0. 000000000	0. 0000000	0. 000000000
1	1	0	1	0
2	2	1	4	2
3	3	3	9	6
4	4	5	16	14
5	5	8	25	27
6	6	12	36	47
7	7	16	49	76
8	8	21	64	115
9	9	27	81	165
10	10	34	100	230
11	11	42	121	310
12	12	50	144	408
13	13	59	169	525
14	14	70	196	664
15	15	81	225	827
16	16	93	256	1016
17	17	106	289	1233
18	18	121	324	1481
19	19	136	361	1763
20	20	152	400	2080
21	21	169	441	2436
22	22	188	484	2832
23	23	207	529	3273
24	24	228	576	3760
25	25	250	625	4297
26	26	273	676	4886
27	27	297	729	5531
28	28	323	784	6234
29	29	350	841	7000
30	30	378	900	7830
31	31	407	961	8729
32	32	438	1024	9699
33	33	470	1089	10745
34	34	504	1156	11870
35	35	539	1225	13077
36	36	575	1296	14370
37	37	613	1369	15753
38	38	653	1444	17230
39	39	694	1521	18804

[1] See footnote at end of table.

TABLE 11.—*Data for computing temperatures in platinum resistance thermometry by the equations* [1]—Continued

$-t$	$-\frac{t}{10^2}$	$-(t-300)\frac{t^2}{10^{10}}$	$\frac{t^2}{10^7}$	$(t-200)\frac{t^2}{10^{10}}$
40	40	736	1600	20480
41	41	780	1681	22261
42	42	826	1764	24153
43	43	873	1849	26158
44	44	922	1936	28281
45	45	972	2025	30527
46	46	1024	2116	32900
47	47	1078	2209	35404
48	48	1134	2304	38044
49	49	1191	2401	40824
50	50	1250	2500	43750
51	51	1311	2601	46826
52	52	1374	2704	50056
53	53	1438	2809	53447
54	54	1505	2916	57002
55	55	1573	3025	60727
56	56	1643	3136	64627
57	57	1715	3249	68707
58	58	1790	3364	72972
59	59	1866	3481	77428
60	60	1944	3600	82080
61	61	2024	3721	86934
62	62	2107	3844	91995
63	63	2191	3969	97268
64	64	2277	4096	102760
65	65	2366	4225	108477
66	66	2457	4356	114423
67	67	2550	4489	120606
68	68	2645	4624	127031
69	69	2742	4761	133703
70	70	2842	4900	140630
71	71	2944	5041	147817
72	72	3048	5184	155271
73	73	3155	5329	162998
74	74	3264	5476	171005
75	75	3375	5625	179297
76	76	3489	5776	187882
77	77	3605	5929	196766
78	78	3723	6084	205956
79	79	3844	6241	215458
80	80	3968	6400	225280
81	81	4094	6561	235428
82	82	4223	6724	245910
83	83	4354	6889	256732
84	84	4488	7056	267902
85	85	4624	7225	279427
86	86	4763	7396	291314
87	87	4905	7569	303570
88	88	5049	7744	316203
89	89	5196	7921	329221

[1] See footnote at end of table.

TABLE 11.—*Data for computing temperatures in platinum resistance thermometry by the equations*[1]—Continued

$-t$	$-\frac{t}{10^2}$	$-(t-300)\frac{t^2}{10^{12}}$	$\frac{t^2}{10^7}$	$(t-200)\frac{t^2}{10^{12}}$
90	90	5346	8100	342630
91	91	5499	8281	356439
92	92	5654	8464	370655
93	93	5812	8649	385287
94	94	5973	8836	400341
95	95	6137	9025	415827
96	96	6304	9216	431751
97	97	6473	9409	448122
98	98	6646	9604	464949
99	99	6821	9801	482239
100	100	7000	10000	500000
101	101	7182	10201	518241
102	102	7366	10404	536971
103	103	7554	10609	556198
104	104	7744	10816	575930
105	105	7938	11025	596177
106	106	8135	11236	616946
107	107	8335	11449	638247
108	108	8538	11664	660089
109	109	8744	11881	682480
110	110	8954	12100	705430
111	111	9167	12321	728947
112	112	9383	12544	753041
113	113	9602	12769	777721
114	114	9825	12996	802997
115	115	10051	13225	828877
116	116	10280	13456	855371
117	117	10513	13689	882489
118	118	10749	13924	910240
119	119	10989	14161	938634
120	120	11232	14400	967680
121	121	11479	14641	997389
122	122	11729	14884	1027770
123	123	11982	15129	1058833
124	124	12239	15376	1090589
125	125	12500	15625	1123047
126	126	12764	15876	1156217
127	127	13032	16129	1190111
128	128	13304	16384	1224737
129	129	13579	16641	1260106
130	130	13858	16900	1296230
131	131	14141	17161	1333118
132	132	14427	17424	1370781
133	133	14717	17689	1409230
134	134	15011	17956	1448475
135	135	15309	18225	1488527
136	136	15611	18496	1529397
137	137	15916	18769	1571097
138	138	16225	19044	1613636
139	139	16539	19321	1657027

[1] See footnote at end of table.

TABLE 11.—*Data for computing temperatures in platinum resistance thermometry by the equations*[1]—Continued

$-t$	$-\frac{t}{10^3}$	$-(t-300)\frac{t}{10^{13}}$	$\frac{t}{10^7}$	$(t-200)\frac{t}{10^{13}}$
140	140	16856	19600	1701280
141	141	17177	19881	1746407
142	142	17502	20164	1792418
143	143	17832	20449	1839326
144	144	18165	20736	1887142
145	145	18502	21025	1935877
146	146	18843	21316	1985543
147	147	19189	21609	2036151
148	148	19538	21904	2087714
149	149	19892	22201	2140243
150	150	20250	22500	2193750
151	151	20612	22801	2248247
152	152	20978	23104	2303746
153	153	21349	23409	2360259
154	154	21724	23716	2417799
155	155	22103	24025	2476377
156	156	22486	24336	2536006
157	157	22874	24649	2596698
158	158	23266	24964	2658466
159	159	23663	25281	2721323
160	160	24064	25600	2785280
161	161	24469	25921	2850351
162	162	24879	26244	2916548
163	163	25294	26569	2983885
164	164	25713	26896	3052373
165	165	26136	27225	3122027
166	166	26564	27556	3192859
167	167	26997	27889	3264882
168	168	27434	28224	3338109
169	169	27876	28561	3412554
170	170	28322	28900	3488230
171	171	28773	29241	3565150
172	172	29229	29584	3643329
173	173	29690	29929	3722779
174	174	30155	30276	3803513
175	175	30625	30625	3885547
176	176	31100	30976	3968893
177	177	31580	31329	4053565
178	178	32064	31684	4139578
179	179	32554	32041	4226945
180	180	33048	32400	4315680
181	181	33547	32761	4405798
182	182	34051	33124	4497312
183	183	34561	33489	4590237
184	184	35075	33856	4684587
185	185	35594	34225	4780377
186	186	36118	34596	4877621
187	187	36648	34969	4976333
188	188	37182	35344	5076529
189	189	37721	35721	5178223
190	0. 000190	0. 000038266	0. 0036100	0. 005281430

[1] The constants R_0, A, B, and C are determined by measurements of resistances at the melting point of ice, the boiling points of water, sulfur, and oxygen, respectively. The powers of 10 used in the computations as coefficients of the functions of t; and of the constants B and C are such as to make the order of magnitude of the constant factors greater than 1 but less than 10 and to effect a simple regulation of decimal points.

TABLE 12.—*Data for computing temperatures in platinum resistance thermometry by the equations* [1]

$$t_2=\frac{[(R_t/R_0)-1]+Bt_1^2}{A+2Bt_1}$$

and

$$t_2=\frac{[(R_t/R_0)-1]+Bt_1^2+E[(t_1/100)-1]t_1^2}{A+2Bt_1+F[(t_1/100)-1]t_1^2}$$

in the ranges of temperature from 0° to 190° C and 0° to −190° C, respectively.

$-t$	$-\frac{t}{10^6}$	$-\left(\frac{t}{100}-1\right)\frac{t^2}{10^6}$	$\frac{t^2}{2\times10^6}$	$\left(\frac{t}{100}-1\right)\frac{t^2}{10^6}$
0	0. 000000	0. 000000000	0. 0000000	0. 000000000
1	1	1	5	1
2	2	4	20	8
3	3	9	45	28
4	4	17	80	67
5	5	26	125	131
6	6	38	180	229
7	7	52	245	367
8	8	69	320	553
9	9	88	405	795
10	10	110	500	1100
11	11	134	605	1477
12	12	161	720	1935
13	13	191	845	2483
14	14	223	980	3128
15	15	259	1125	3881
16	16	297	1280	4751
17	17	338	1445	5748
18	18	382	1620	6882
19	19	430	1805	8162
20	20	480	2000	9600
21	21	534	2205	11206
22	22	590	2420	12991
23	23	651	2645	14965
24	24	714	2880	17142
25	25	781	3125	19531
26	26	852	3380	22146
27	27	926	3645	24997
28	28	1004	3920	28099
29	29	1085	4205	31462
30	30	1170	4500	35100
31	31	1259	4805	39026
32	32	1352	5120	43254
33	33	1448	5445	47796
34	34	1549	5780	52667
35	35	1654	6125	57881
36	36	1763	6480	63452
37	37	1876	6845	69395
38	38	1993	7220	75723
39	39	2114	7605	82453

[1] See footnote at end of table.

TABLE 12.—*Data for computing temperatures in platinum resistance thermometry by the equations* [1]—Continued

$-t$	$-\frac{t}{10^3}$	$-\left(\frac{t}{100}-1\right)\frac{t}{10^3}$	$\frac{t^2}{2\times10^3}$	$\left(\frac{t}{100}-1\right)\frac{t}{10^3}$
40	40	2240	8000	89600
41	41	2370	8405	97179
42	42	2505	8820	105205
43	43	2644	9245	113695
44	44	2788	9680	122665
45	45	2936	10125	132131
46	46	3089	10580	142111
47	47	3247	11045	152620
48	48	3410	11520	163676
49	49	3577	12005	175297
50	50	3750	12500	187500
51	51	3928	13005	200303
52	52	4110	13520	213724
53	53	4298	14045	227782
54	54	4491	14580	242495
55	55	4689	15125	257881
56	56	4892	15680	273961
57	57	5101	16245	290753
58	58	5315	16820	308277
59	59	5535	17405	326553
60	60	5760	18000	345600
61	61	5991	18605	365439
62	62	6227	19220	386091
63	63	6469	19845	407577
64	64	6717	20480	429916
65	65	6971	21125	453131
66	66	7231	21780	477243
67	67	7497	22445	502274
68	68	7768	23120	528246
69	69	8046	23805	555180
70	70	8330	24500	583100
71	71	8620	25205	612028
72	72	8916	25920	641987
73	73	9219	26645	672999
74	74	9528	27380	705090
75	75	9844	28125	738281
76	76	10166	28880	772598
77	77	10494	29645	808063
78	78	10830	30420	844703
79	79	11171	31205	882540
80	80	11520	32000	921600
81	81	11875	32805	961908
82	82	12238	33620	1003490
83	83	12607	34445	1046370
84	84	12983	35280	1090575
85	85	13366	36125	1136131
86	86	13757	36980	1183064
87	87	14154	37845	1231401
88	88	14559	38720	1281167
89	89	14971	39605	1332391

[1] See footnote at end of table.

TABLE 12.—*Data for computing temperatures in platinum resistance thermometry by the equations* [1]—Continued

$-t$	$-\frac{t}{10^2}$	$-\left(\frac{t}{100}-1\right)\frac{t}{10^2}$	$\frac{t^2}{2\times10^4}$	$\left(\frac{t}{100}-1\right)\frac{t^2}{10^4}$
90	90	15390	40500	1385100
91	91	15817	41405	1439321
92	92	16251	42320	1495081
93	93	16693	43245	1552409
94	94	17142	44180	1611333
95	95	17599	45125	1671881
96	96	18063	46080	1734083
97	97	18536	47045	1797966
98	98	19016	48020	1863560
99	99	19504	49005	1930895
100	100	20000	50000	2000000
101	101	20504	51005	2070905
102	102	21016	52020	2143640
103	103	21536	53045	2218236
104	104	22065	54080	2294723
105	105	22601	55125	2373131
106	106	23146	56180	2453493
107	107	23699	57245	2535839
108	108	24261	58320	2620201
109	109	24831	59405	2706611
110	110	25410	60500	2795100
111	111	25997	61605	2885701
112	112	26593	62720	2978447
113	113	27198	63845	3073371
114	114	27811	64980	3170504
115	115	28434	66125	3269881
116	116	29065	67280	3371535
117	117	29705	68445	3475500
118	118	30354	69620	3581810
119	119	31013	70805	3690498
120	120	31680	72000	3801600
121	121	32357	73205	3915150
122	122	33042	74420	4031183
123	123	33738	75645	4149733
124	124	34442	76880	4270838
125	125	35156	78125	4394531
126	126	35880	79380	4520850
127	127	36613	80645	4649829
128	128	37356	81920	4781507
129	129	38108	83205	4915918
130	130	38870	84500	5053100
131	131	39642	85805	5193090
132	132	40424	87120	5335926
133	133	41215	88445	5481644
134	134	42017	89780	5630283
135	135	42829	91125	5781881
136	136	43651	92480	5936476
137	137	44483	93845	6094107
138	138	45325	95220	6254811
139	139	46177	96605	6418629

[1] See footnote at end of table.

TABLE 12.—*Data for computing temperatures in platinum resistance thermometry by the equations*[1]—Continued

$-t$	$-\frac{t}{10^2}$	$-\left(\frac{t}{100}-1\right)\frac{t}{10^2}$	$\frac{t^2}{2\times10^2}$	$\left(\frac{t}{100}-1\right)\frac{t}{10^2}$
140	140	47040	98000	6585600
141	141	47913	99405	6755763
142	142	48797	100820	6929157
143	143	49691	102245	7105823
144	144	50596	103680	7285801
145	145	51511	105125	7469131
146	146	52437	106580	7655855
147	147	53374	108045	7846012
148	148	54322	109520	8039644
149	149	55280	111005	8236793
150	150	56250	112500	8437500
151	151	57231	114005	8641807
152	152	58222	115520	8849756
153	153	59225	117045	9061390
154	154	60239	118580	9276751
155	155	61264	120125	9495881
156	156	62300	121680	9718825
157	157	63348	123245	9945625
158	158	64407	124820	10176325
159	159	65478	126405	10410969
160	160	66560	128000	10649600
161	161	67654	129605	10892263
162	162	68759	131220	11139003
163	163	69876	132845	11389865
164	164	71005	134480	11644892
165	165	72146	136125	11904131
166	166	73299	137780	12167627
167	167	74464	139445	12435426
168	168	75640	141120	12707574
169	169	76829	142805	12984116
170	170	78030	144500	13265100
171	171	79243	146205	13550572
172	172	80468	147920	13840579
173	173	81706	149645	14135167
174	174	82956	151380	14434386
175	175	84219	153125	14738281
176	176	85494	154880	15046902
177	177	86781	156645	15360295
178	178	88082	158420	15678511
179	179	89394	160205	16001596
180	180	90720	162000	16329600
181	181	92058	163805	16662572
182	182	93410	165620	17000562
183	183	94774	167445	17343618
184	184	96151	169280	17691791
185	185	97541	171125	18045131
186	186	98945	172980	18403688
187	187	100361	174845	18767513
188	188	101791	176720	19136655
189	189	103234	178605	19511167
190	0. 000190	0. 000104690	0. 0180500	0. 019891100

[1] The constants R_0, A, B, and C are determined by measurements of resistances at the melting point of ice, the boiling points of water, sulfur, and oxygen, respectively. E and F are equal to $264C$ and $364C$, respectively. The powers of 10 used in the computations as coefficients of the functions of t_1, and of the constants B, E, and F are such as to make the order of magnitude of the constant factors greater than 1 but less than 10 and to effect a simple regulation of decimal points.

Set decimal point indicators at corresponding positions on the keyboard and middle dial of a calculating machine equivalent to the Marchant Model M. Set the value of A in the keyboard in its proper position for the decimal point and add it into the middle dial. This clears the keyboard. Set the value of $10^{-6}t_1$ in the keyboard properly with respect to its decimal point and multiply, by 2×10^6B. This operation adds the product, $2Bt_1$, to A in the middle dial. Bring the carriage back to its original position, place the value of $10^{-12}(4t_1-300)t_1^2$ taken from table 11 if equation 12 is used, or the value of $10^{-9}[(t_1/100)-1]t_1^2$ taken from table 12 if equation 14 is used, in the keyboard with proper account of the decimal point, multiply by $10^{12}C$ for equation 12, or by 10^9F for equation 14. This operation adds the third term of the denominator to the sum of the first two and shows the value of the whole denominator in the middle dial. Record this value on paper and clear the dials of the machine. The numerator is next obtained in the same manner but left in the middle dial while the denominator is set in the keyboard. Automatic division now yields the temperature correct to the nearest millidegree. With practice, the computation of a temperature, exclusive of the calculation of $(R_t/R_0)-1$, can be made by this procedure in less than 2 minutes.

The powers of 10 used in the computations as coefficients of the functions of t_1 and of the constants B and C are such as to make the order of magnitude of the constant factors greater than 1 but less than 10 and to effect a simple regulation of decimal points. In table 11, for use with equation 12, the following are tabulated:

$10^{-6}t_1$ to be multiplied by 2×10^6B to obtain $2Bt_1$, as 2×10^6B is approximately 1.2.

$10^{-12}(4t_1-300)t_1^2$ and $10^{-12}(3t_1-200)t_1^2$ to be multiplied by $10^{12}C$ to obtain $C(4t_1-300)t_1^2$ and $C(3t_1-200)t_1^2$, since $10^{12}C$ is approximately 4.4.

$10^{-7}t_1^2$ to be multiplied by 10^7B to obtain Bt_1^2, as 10^7B is approximately 6.

In table 12, for use with equation 14, the tabulation is analogous. With proper regard for signs, columns 2 and 4 of table 11 or table 12 can be used to calculate temperatures in the upper range from 0° to 190° C, if the table for computations of temperatures below 0° C is complete. These columns can be extended to 660° C, or a table of squares can be used.

Computations made with these modified fundamental equations involve the ratio of R_t to R_0, both of which should therefore be measured with the same bridge. This ratio will be practically the same for the same temperature with any calibrated bridge, provided the calibration of a given bridge is consistent, i. e., of about the same fractional error in all the dials. The fundamental constants are assumed to be given correctly, i. e., the thermometer must have a proper calibration and this, of course, is true no matter what method of computation is used. The steam point does not appear in the equations and can even be eliminated from the calibration of the thermometer by the use of another fixed point in a suitable region of the temperature scale, such as the freezing point of benzoic acid, or by comparison with a thermometer which has been given a primary calibration.

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pH OF AQUEOUS MIXTURES OF POTASSIUM DIHYDROGEN PHOSPHATE AND DISODIUM HYDROGEN PHOSPHATE AT 0° TO 60° C

By Roger G. Bates and S. F. Acree

ABSTRACT

A method is suggested for computing the pH of phosphate buffers from electromotive-force measurements of cells without liquid junction. Each of the 33 buffer solutions studied was prepared from equal molal quantities of potassium dihydrogen phosphate and disodium hydrogen phosphate. The solutions were divided into five series with respect to the amount of sodium chloride added. The ratios of the molality of each buffer salt to that of sodium chloride in the five series were about 1, 2, 3, 8, and 10. The pH values were computed from measurements of cells with hydrogen electrodes and silver–silver-chloride electrodes by a procedure that involves extrapolation of a function of the emf to zero concentration of sodium chloride.

The values of the second dissociation constant of phosphoric acid given in an earlier paper (RP1524) were confirmed. The mean values of pK, the negative of the common logarithm of the second dissociation constant, are given as a function of absolute temperature, T, by the equation

$$\mathrm{p}K = 2073.0/T - 5.9884 + 0.020912T$$

between $T=273.16$ and $T=323.16$ (0° to 50° C). Equations are given to express the change of pH with molality of sodium chloride. The pH values from 0° to 60° C of eight phosphate buffers without chloride are listed. The densities of the buffers were determined. At 25° C, the pH of buffers containing equal molal quantities of potassium dihydrogen phosphate and of disodium hydrogen phosphate is given by the equations

$$\mathrm{pH} = 7.162 + 2.18\ m - 2.237\sqrt{m}$$

and

$$\mathrm{pH} = 7.169 + 2.39\ c - 2.324\sqrt{c},$$

where m and c, the molality and the molar concentration of each buffer salt, lie between 0.005 and 0.1.

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I. INTRODUCTION

Aqueous mixtures of primary and secondary phosphates have found extensive use for the control of pH in the region near neutrality. When the molal amounts of the two phosphates are approximately equal, buffer solutions with pH between 6.5 and 7.0 are obtained. The pH is relatively insensitive to contamination of the solution with carbon dioxide from the air, or with small amounts of alkali, and changes only 0.1 unit when the solution is diluted to twice its volume with pure water.

It was shown in an earlier paper [1][1] that potassium dihydrogen phosphate and disodium hydrogen phosphate are well suited by ease of purification, stability, and lack of pronounced hygroscopicity to the preparation of standard buffers of constant and reproducible pH. The equimolal mixture of these two salts was chosen for detailed study. The purpose of this investigation was twofold: to determine the pH of a series of phosphate buffer standards, and to study the effect of sodium chloride on the thermodynamic properties of the phosphate buffer system. The study of salt effects on the behavior of indicators and buffers has been the subject of earlier communications from this Bureau [2, 3, 4, 5].

In the past, pH values assigned to phosphate buffers have been based upon emf measurements of cells which involved liquid junctions [6, 7, 8]. The experimental and theoretical difficulties caused by the liquid junction have been well recognized, and it has been suggested [9, 10, 11] that pH be defined in terms of cells without liquid junction. The experimental difficulties are thereby removed to a large extent, but the uncertainty in evaluating the potential at the liquid junction remains in the guise of its counterpart, the enigma of the single-ion activity. In either case, a non-thermodynamic assumption must be made, and the pH scale is somewhat arbitrary in character. When strong acids and bases as well as buffered solutions are to be used, however, a consistent scale based on cells with liquid junction is not readily achieved [8, 11a].

In previous work by the authors, the second dissociation constant of phosphoric acid was evaluated from emf measurements of cells without liquid junction. Certain assumptions were made to relate the activity coefficient of chloride ion to an observed activity function, and pH values were computed for the mixtures of phosphate and chloride salts. A change in the ratio of chloride to buffer salt alters the pH of the buffer, however, in a hitherto unknown manner. In this investigation, the effect of the sodium chloride on the activity coefficients has been studied, and the pH of phosphate buffers in the absence of sodium chloride has been estimated.

II. EXPERIMENTAL PROCEDURE

The solutions were prepared by the dilution of eight stock solutions with conductivity water. Each stock solution was prepared from the proper weights of pure potassium dihydrogen phosphate, disodium hydrogen phosphate, sodium chloride, and water. The dilutions were made in an atmosphere from which carbon dioxide had been removed.

[1] Figures in brackets indicate the literature references at the end of this paper.

The concentration of each component was expressed on the weight basis and was thought to be correct to 0.01 percent. Dissolved oxygen was removed from each solution by means of nitrogen, which had been purified by passage through a tower of soda-lime and over copper heated to 500° C. The gas was bubbled through each solution for 3 hours before the final weighings were made.

The silver–silver-chloride electrodes were of the thermal-electrolytic type (Harned's type 2 [12]). About 15 mg of the silver formed on each electrode (usually about 70 mg) was converted to silver chloride. Both the hydrogen electrodes and the silver–silver-chloride electrodes were freshly prepared before each series of experiments was begun. The latter were intercompared in a 0.05-*m* solution of hydrochloric acid and only those differing from the mean value by 0.06 mv or less were used. Experience showed that a similar intercomparison of hydrogen electrodes was unnecessary.

Each series of experiments ordinarily was completed within 72 hours after the cells were filled. Initial and final measurements were made at 25° C. The thermometer, standard cell, and potentiometer had been calibrated recently. The ice point of the thermometer was usually redetermined before each series of experiments was started. Other experimental details are given in an earlier paper [1].

1. MATERIALS

Potassium dihydrogen phosphate and disodium hydrogen phosphate were purified by recrystallization from water, dried at 110° and 130° C, respectively, and used as the anhydrous salts. The secondary salt was first dried for a time at room temperature in air and in vacuum. In this way, fusion of the hydrated salt at 130° C was avoided. Samples of these two salts, prepared by triple crystallization of reagent grade salts which conformed to specifications of the American Chemical Society, were analyzed by the Reagents and Platinum Metals Section of this Bureau. The assays of potassium dihydrogen phosphate and of disodium hydrogen phosphate were, respectively, 100.003 and 99.995 percent. The secondary salt was shown to contain less than 0.01 percent of carbonate.

Sodium chloride, "special grade," was precipitated from a saturated aqueous solution with dry hydrogen chloride, prepared according to the directions of Sweeney [13], and fused in platinum to remove water and occluded acid, as recommended by Richards and Wells [14]. It was broken into large lumps and bottled without grinding. The salt was not strictly neutral, as Richards and Wells found theirs to be. A measure of its alkalinity was made by titration of a sample of 11 g of the salt to both the phenolphthalein and methyl-orange end points with a solution of hydrochloric acid. The amount of acid required indicated the presence of 0.008 percent of sodium hydroxide by weight. As this impurity would cause an error in electromotive force of less than 0.01 mv, or considerably less than the experimental error, no further purification of the salt was undertaken.

The conductance of the water used in the preparation of the solutions was approximately 0.5×10^{-6} mho. Before the water was used, a stream of air freed of carbon dioxide was bubbled through it for 18 to 24 hours. In an experiment to test the removal of dissolved carbon dioxide by this method, eight liters of water having an initial conductance of 0.44×10^{-6} mho remained in the receiver for 2 months. The conductance rose to 0.97×10^{-6} mho during this time but fell to 0.57×10^{-6} mho when carbon dioxide-free air was bubbled through the water overnight.

2. RESULTS OF EMF MEASUREMENTS

The electromotive forces, E_t, of the cell $Pt|H_2|KH_2PO_4$, (m_1); Na_2HPO_4, (m_1); NaCl, $(m_2)|AgCl|Ag$ are given in table 1. These values have been corrected as usual to 1 atm of hydrogen. In each solution, the stoichiometric molalities (m_1) of the primary and secondary phosphate salts were equal. Furthermore, it can be shown that the concentrations of primary and secondary phosphate anions are substantially equal (within 0.01 percent) to the stoichiometric molalities of the corresponding phosphate salts. The molalities of the components of the solution are given in the second and third columns of the table. The solutions are divided into five series. In series A, B, C, D, and E the ratios of the molality of each buffer salt to the molality of sodium chloride were respectively 1.00, 1.92, 3.21, 8.20, and 9.90.

The molalities of solutions A5 and A5a were identical. Solution A5 was saturated with hydrogen, however, before the cells were filled, and A5a was saturated with nitrogen in the same manner as was each of the other buffers. The emf values agree satisfactorily. The data recorded for solutions D2 and D6 are the average values of two cells. The mean differences between the two cells were 0.03 mv (for D2) and 0.08 mv (for D6).

The values at 25° C, in general, are somewhat more reliable than those listed for the other temperatures, by virtue of the threefold check obtained at this reference temperature. The initial equilibrium values at 25° C were uniformly in agreement with those recorded at the conclusion of the low-temperature series. When the molality of the buffer was less than 0.005 or that of the chloride less than 0.002, however, the final values at the same temperature often differed from the initial data by 0.02 to 0.03 percent of the emf (about 0.2 mv). In such cases, the final measurement was disregarded in assigning the value to the cell at 25° C. It was recognized, further, that at least a part of this error possibly resides in the values at the highest temperatures. It will be seen later that the deviations from the mean of the second dissociation constant calculated from the experimental results at 50°, 55°, and 60° C are somewhat larger than those at the lower temperatures.

TABLE 1.—*Electromotive forces of cells containing mixtures of phosphate buffers with sodium chloride*

TABLE 1.—*Electromotive forces of cells containing mixtures of phosphate buffers with sodium chloride*

Solution number	KH_2PO_4= Na_2HPO_4 (m)	NaCl (m)	$E_{25°}$		$E_{30°}$		$E_{35°}$		$E_{40°}$		$E_{45°}$		$E_{50°}$		$E_{55°}$		$E_{60°}$		$E_{65°}$	
	Molality	*Molality*	*Int.*	*v*	*Int.*	*v*	*Int.*	*v*	*Int.*	*v*	*Int.*	*v*	*Int.*	*v*	*Int.*	*v*	*Int.*	*v*	*Int.*	*v*
A1	0.06568	0.06568								0.69706										
A2	.03896	.03896	0.69697		0.70538					.71392		0.72247		0.73114				0.73979		
A3	.02873	.02875					0.71898			.72342		.72778								0.75468
A4	.02820	.02822	0.70191		0.71030					.72407		.72844		.73293		.74204		.74675		.75594
A5	.02157	.02158	.70235		.71100		.71923		.71966					.73748						
A5a	.02157	.02158																		
			.71451				.72339			.73246		.74161		.75080						
			.71451				.72334			.73248										
A6	.02000	.02000								.73481		.74021		.74954		.75869		.76835		.76835
A7	.019412	.019422	.71303						.73694		.73559		.74102		.74671		.75517		.76405	
A8	.018981	.018999			.72187					.73635				.75045						.76046
A9	.013668	.013672	.71366		.72274		.72728		.73170		.74638		.75618		.76618		.76600		.77591	
A10	.012317	.012328	.72586				.73885			.74494		.74950								
A11	.009647	.009651	.73536		.74005				.75184		.75683									
A12	.007384	.007391	.73246		.74207		.74892		.75895		.76398		.76917		.77433		.78461		.78996		.78517
A13	.007040	.007043	.74400		.75095		.75302		.76103		.76616		.77133		.77653		.78171		.79219	
A14	.004657	.004660	.73212		.76226				.77278		.77819		.78361		.78903		.79443		.80533	
B1	.06628	.05170	.68172		.68376		.68967		.69359		.69766		.70158		.70560		.70962		.71375		.71785		.72192		.72600		.73018
B2	.05478	.02853	.69648		.70385		.70606		.71228		.71663		.72057		.72526		.72976		.73430		.73870		.74315		.74762		.75213
B3	.03073	.01000	.71627		.72084		.72333		.72987		.73454		.73912		.74376		.74866		.75346		.75829		.76309		.76799		.77275
B4	.019063	.009921	.72998		.73454		.73925		.74403		.74897		.75381		.75890		.76393		.76900		.77407		.77913		.78430		.78935
C1	.09928	.03067	.69422		.69851		.70264		.70683		.71100		.71528		.71947		.72380		.72825		.73263		.73702		.74136		.74581
C2	.05143	.01606	.71374		.71826		.72252		.72711		.73170		.73637		.74104		.74586		.75040		.75514		.75993		.76464		.76948
C3	.02601	.008411	.73217		.73709		.74163		.74669		.75165		.75654		.76144		.76667		.77176		.77687		.78197		.78708		.79227
D1	.08250	.010026	.72249		.72715		.73186		.73649		.74118		.74597		.75083		.75558		.76043		.76524		.77005		.77495		.77980
D2	.06265	.007614	.73065		.73545		.74026		.74506		.74991		.75489		.75979		.76471		.76971		.77460		.77966		.78466		.78962
D3	.05571	.006771	.73401		.73871		.74302		.74850		.75338		.75845		.76344		.76844		.77346		.77851		.78355		.78857		.79363
D4	.04935	.005998	.73751		.74240		.74738		.75230		.75722		.76227		.76740		.77248		.77761		.78273		.78785		.79292		.79810
D5	.04277	.005199	.74159		.74654		.75167		.75668		.76162		.76690		.77197		.77714		.78233		.78753		.79272		.79791		.80309
D6	.03079	.003742	.75109		.75623		.76146		.76664		.77184		.77715		.78258		.78772		.79309		.79843		.80381		.80915		.81455
D7	.017007	.002067	.76745		.77285		.77833		.78380		.78936		.79496														
D8	.010457	.0012709	.78083		.78646		.79219		.79792		.80367		.80954														
E1	.09928	.010012	.72144		.72616		.73073		.73544		.74017		.74491		.74964		.75445		.75930		.76418		.76902		.77389		.77880
E2	.08802	.008834	.74937		.75461		.75970		.76480		.77006		.77531		.78052		.78593		.79133		.79673		.80215		.80752		.81297
E3	.017596	.0017745	.77074		.77639		.78180		.78732		.79296		.79881		.80438		.81002		.81580		.82159		.82737		.83313		.83895

[a] Solution saturated with hydrogen.
[b] Solution saturated with nitrogen.

3. SECOND DISSOCIATION CONSTANT OF PHOSPHORIC ACID AND RELATED THERMODYNAMIC QUANTITIES

The calculation of the second dissociation constant of phosphoric acid from the data of table 1 was made in the manner outlined in the earlier paper.[2] As shown in figure 1, a value of 4.4 A for a^*, the ion-size parameter, gave the best straight-line extrapolation of pK', the negative of the common logarithm of the "apparent" dissociation constant, to zero ionic strength for series D as well as for series A at 25° C, although the ratio of chloride molality to molality of buffer salt was only one-eighth as large. The computation of pK' was made, as before, by use of the equation

$$pK' = (E - E^\circ)/k + \log\ (m_{H_2PO_4} m_{Cl}/m_{HPO_4}) + 2A\sqrt{\mu}/(1 + Ba^*\sqrt{\mu}), \quad (1)$$

where E° is the standard potential of the cell, μ is the ionic strength, and a^* and β^* are considered to be related to the ion-size parameters, a_i, and β values characteristic of the chloride and phosphate anions. This expression has been found to yield values of pK' that are a linear function of ionic strength.

The uncertainty in establishing a^* for series D is about 0.2 A. The uniform character of the measurements of the series A solutions at 25° C, however, makes possible a more accurate evaluation of a^* for this series than can be made for the others. Fortunately, however, the pH values calculated for the phosphate buffer are but slightly affected by a change of 0.2 A in a^*, as will be shown in the following section. This value of a^* is considerably larger than 3.8 A found to give the best representation for mixtures of sodium phosphates and also for a mixture of potassium dihydrogen phosphate, disodium hydrogen phosphate, and sodium chloride in which the molal proportions were 3:2:3 [1].

In accord with previous experience with mixtures of sodium phosphates, it was found that the value of a^* increased slowly with rise of temperature, whereas β^*, the slope of the plot of pK' as a function of ionic strength, remained substantially constant or decreased slowly. As can be seen in figure 2, where pK' from all five series at 25° C is plotted as a function of ionic strength, the β^* slope decreases as the ratio of molalities of sodium chloride to buffer salt is decreased. Since too few solutions in series B, C, and E were studied to provide sufficient data for unambiguous extrapolation, their lines have been drawn to a common intercept which represents the mean value of pK computed analytically from the 10 experimental points.

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[2] The newer values of $k = 2.3036RT/F$ and of the constants A and B of the Debye-Hückel equation were employed [15]. In this paper, K represents the thermodynamic second dissociation constant, and K' the false, "apparent" constant computed with the use of any arbitary activity-coefficient term.

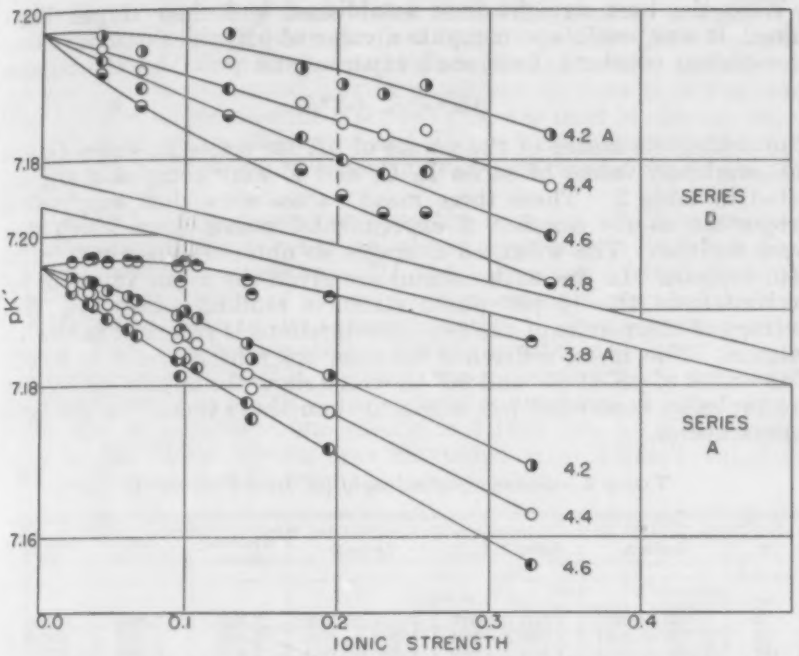

FIGURE 1.—pK *at 25° C for various values of a* plotted as a function of ionic strength.*

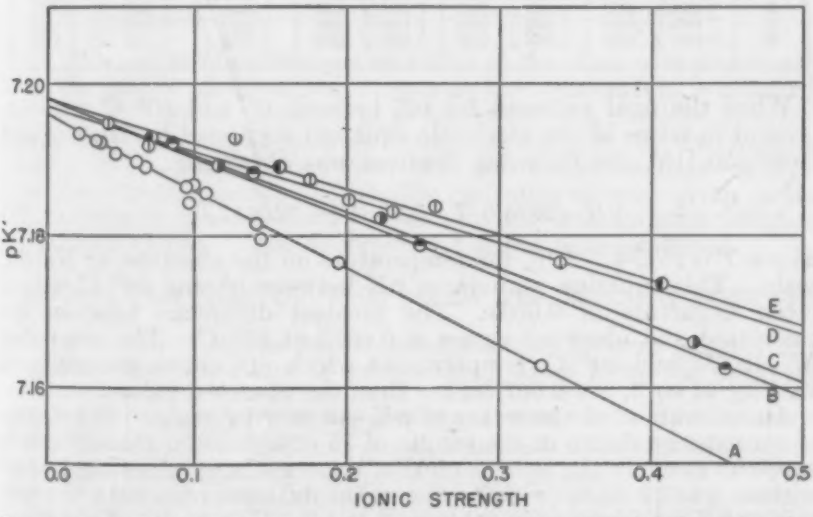

FIGURE 2.—pK' *at 25° C for buffers of series A, B, C, D, and E plotted as a function of ionic strength.*

With the best straight lines established and their slopes determined, it was possible to compute a value of pK, the thermodynamic dissociation constant, from each experimental point by the relation

$$pK = pK' + \beta^* \mu. \quad (2)$$

The arithmetic means of the values of pK for series A, series D, and the combined values of series B, C, and E were computed and are listed in table 2. These three mean values were then weighted in proportion to the number of experimental points from which they were derived. The weighted averages so obtained are given in the fifth column. In the sixth column are given the mean values of pK derived from the 42 phosphate mixtures studied earlier [1]. The average of the results of the two investigations is recorded in the last column. The mean difference between columns 5 and 6 is 0.0011. The values of pK at 55° and 60° C, which show the largest differences, are probably somewhat less accurate than those found for the lower temperatures.

TABLE 2.—*Summary of values of* pK *from 0° to 60° C*

t	Series A	Series B, C, E	Series D	Weighted mean	pK (RP1524)	Average pK
°C						
0	7.3123 ±0.0007	7.3124 ±0.0007	7.3128 ±0.0008	7.3125	7.3138	7.3131
5	7.2824 ± .0011	7.2826 ± .0004	7.2815 ± .0014	7.2822	7.2812	7.2817
10	7.2526 ± .0013	7.2536 ± .0009	7.2543 ± .0014	7.2535	7.2540	7.2537
15	7.2321 ± .0010	7.2317 ± .0006	7.2321 ± .0011	7.2320	7.2304	7.2312
20	7.2125 ± .0014	7.2141 ± .0008	7.2129 ± .0010	7.2132	7.2128	7.2130
25	7.1959 ± .0005	7.1985 ± .0006	7.1978 ± .0011	7.1972	7.1980	7.1976
30	7.1880 ± .0009	7.1886 ± .0007	7.1889 ± .0005	7.1885	7.1897	7.1891
35	7.1844 ± .0009	7.1850 ± .0013	7.1840 ± .0005	7.1845	7.1854	7.1850
40	7.1787 ± .0017	7.1821 ± .0022	7.1794 ± .0007	7.1802	7.1816	7.1809
45	7.1799 ± .0012	7.1820 ± .0019	7.1799 ± .0007	7.1808	7.1810	7.1809
50	7.1804 ± .0023	7.1846 ± .0023	7.1818 ± .0007	7.1824	7.1838	7.1831
55	7.1874 ± .0019	7.1883 ± .0024	7.1830 ± .0007	7.1865	7.1875	7.1870
60	7.1927 ± .0025	7.1955 ± .0027	7.1897 ± .0007	7.1930	7.1958	7.1944

When the final averages for pK between 0° and 50° C were expressed in terms of the quadratic equation suggested by Harned and Robinson [16], the following function was obtained:

$$pK = 2073.0/T - 5.9884 + 0.020912T, \quad (3)$$

where T is t° C+273.16, the temperature on the absolute, or Kelvin, scale. This equation reproduces pK between 0° and 50° C with a mean departure of 0.0007. The greatest difference between the calculated and observed values is 0.0023 at 35° C. The computed pK at 55° and 60° C, temperatures which are above the range of validity of eq 3, are 0.007 higher than the observed values.

An estimate of the accuracy of pK can now be made. The degree of consistency shown in the results of 75 experimental measurements supports strongly the conclusion that these average values are precise within ±0.002 unit, or twice the mean difference between the two sets of pK values given in columns 5 and 6. The purity of the phosphate salts was such that no appreciable uncertainty can justifiably be attributed to that source. The slight alkalinity of the sodium chloride would cause all of the values to be too high by only 0.0001

unit. The $E°$ values of Harned and Ehlers [17] seem to be reliable to about 0.05 mv, which corresponds to 0.0009 in pK. A more recent calculation of $E°$ from their data [18] confirms this view, as far as the extrapolation is concerned. It is important to note that the same type of silver–silver-chloride electrode [12] was used in this investigation and in the work of Harned and Ehlers. By summation of these possible errors, a maximum uncertainty of ± 0.003 unit can be assigned to pK.

Since eq 3 differs somewhat from the equation which represented most successfully the series of pK values given in column 6 as a function of absolute temperature [1],[3] the quantities derived from the temperature coefficient of the dissociation constant were recalculated from the parameters of the revised equation. They are compared in table 3 with the corresponding quantities obtained from the emf measurements of Nims [19], and with a direct calorimetric determination of $\Delta H°$ by Pitzer [20]. The constants are given in international joules and in calories;[4] one calorie is 4.1833 int. j. The entropy value in the third column was computed from Pitzer's value for $\Delta H°$, together with $\Delta F°$ from this investigation.

TABLE 3.—*Thermodynamic constants for the dissociation of* $H_2PO_4^-$ *at 25° C*

		Nims (emf)	Pitzer (calorimetry)	This investigation
pK		7.205[5]		7.197[5]
$\Delta F°$	cal/mole	9,830		9,822
	int. j/mole	41,122		41,068
$\Delta H°$	cal/mole	825	800 ±80	979
	int. j/mole	3,451	3,347 ±335	4,095
$\Delta S°$	cal/deg mole	−30.2	−30.3	−29.6
	int. j/deg mole	−126.3	−126.8	−123.8
$\Delta C°_p$	cal/deg mole	−45		−57
	int. j/deg mole	−188		−238

In the absence of unforeseen reactions at the electrodes which may alter the emf in an abnormal manner as the temperature is changed, $\Delta H°$ should have an uncertainty of about 300 int. j/mole, $\Delta S°$ might be in error by 0.9 int. j/degree mole, and $\Delta C°_p$ by 25 int. j/degree mole.[5] It is apparent, however, that the difference between $\Delta H°$ from calorimetric data and from the emf measurement given in the last column is greater than the sum of the uncertainties assigned to the two values. This discrepancy has not been explained.

III. CALCULATION OF THE pH OF PHOSPHATE BUFFERS

If the mass-law expression for the equilibrium between primary and secondary phosphate ions is written in its exact form, the following

[3] This equation was pK=1979.5/T−5.3541+0.019840T. The values found by Nims [19] from 20° and 50° C are expressed by pK=1651.9/T−3.2703+0.016555T.

[4] Quantities of energy in chemical thermodynamics are measured in joules, and the arbitrary conversion to artificial calories has little to recommend it. The eventual abandonment of the calorie as a unit of energy has been urged by Smith and Taylor [21], Mueller and Rossini [22], and others.

[5] These uncertainties were estimated from the probable limit of error (0.002 unit) assigned to pK. If pK at 15° C were too low by 0.002 unit and pK at 35° too high by the same margin, the stated errors would be included in the values of the thermodynamic constants at 25° C.

equation for the pH of any mixture of potassium dihydrogen phosphate and disodium hydrogen phosphate is obtained:

$$\mathrm{pH}=\mathrm{p}K-\log\frac{m_{\mathrm{H_2PO_4}}}{m_{\mathrm{HPO_4}}}-\log\frac{f_{\mathrm{H_2PO_4}}}{f_{\mathrm{HPO_4}}}. \tag{4}$$

In order to estimate the last term of eq 4, an equation of the Hückel form was assumed to express the change of each ionic activity coefficient in the mixture with respect to ionic strength, as follows:

$$-\log f_i=\frac{Az_i^2\sqrt{\mu}}{1+Ba_i\sqrt{\mu}}-\beta_i\mu. \tag{5}$$

In eq 5, z_i is the valence of the ion, and a_i and β_i are parameters characteristic of the ionic species i in the mixture.

If eq 5 correctly represents the change of each ionic activity coefficient with respect to the ionic strength, it is possible to derive the relationship between a^* and a_1, a_2, and a_3, where the subscripts 1, 2, and 3 refer respectively to the anions H_2PO_4, HPO_4, and Cl.

$$a^*=\frac{(4a_2-a_1-a_3)+(3a_1a_2-2a_1a_3+3a_2a_3)B\sqrt{\mu}+2a_1a_2a_3B^2\mu}{2+(3a_1-2a_2+3a_3)B\sqrt{\mu}+(4a_1a_3-a_1a_2-a_2a_3)B^2\mu}. \tag{6}$$

This derivation is accomplished by combining expressions of the form of eq 5 for the activity coefficients of the three anions according to the formula $(\log f_{\mathrm{H_2PO_4}}-\log f_{\mathrm{HPO_4}}+\log f_{\mathrm{Cl}})$, and equating the result to $2A\sqrt{\mu}/(1+Ba^*\sqrt{\mu})+\beta^*\mu$, which is found by experiment to represent satisfactorily the quantity $\log\ (f_{\mathrm{H_2PO_4}}\ f_{\mathrm{Cl}}/f_{\mathrm{HPO_4}})$.

Consideration of eq 6 shows that a^* is totally independent of ionic strength only when $a_1=a_2=a_3=a^*$. When the values of the ion-size parameter for the three ions are different, a^* is an insensitive function of μ. As the ionic strength approaches zero, a^* approaches $(4a_2-a_1-a_3)/2$ as a limit. At infinite ionic strength, a^* is $2a_1a_2a_3/(4a_1a_3-a_1a_2-a_2a_3)$. When the ratios of the ions were fixed, no variation of a^* with ionic strength larger than the experimental error could be detected. This invariance would be observed if the ion-size parameters for the three ions were equal. For many combinations of different values of a_i lying between 3 and 5 A, however, the change of a^* over very large ranges of ionic strengths can be shown to be so small as not to be discernible.

Examination of eq 6 in the light of the behavior of the term $\log(f_{\mathrm{H_2PO_4}}f_{\mathrm{Cl}}/f_{\mathrm{HPO_4}})$ with changing buffer ratio, however, reveals no explanation of the observed change of a^* as the relative amounts of the primary and secondary phosphates are varied at a constant ionic strength, provided that the individual a_i values are considered to be constants. It seems reasonable to assume that the ionic parameters are not equal and that their contributions to a^* are weighted in some manner, not shown in eq 6, according to the contributions of the respective ions to the ionic strength. The limiting value of a^*, or a°, as m_{NaCl}/μ approaches zero at a constant ratio of the phosphate salts would then be little influenced by the individual characteristics of

the chloride ion and determined chiefly by those of the phosphate anions.

In the light of eq 5, the slope β^* can be considered to be a combination of the values of β_i for primary phosphate ion, secondary phosphate ion, and chloride ion: $\beta^* = \beta_{H_2PO_4} - \beta_{HPO_4} + \beta_{Cl}$. If the contribution of β_{Cl} varies in some direct manner with the fractional contribution of sodium chloride to the total ionic strength, the limit of β^* for the equimolal phosphate buffer in the absence of sodium chloride, $(\beta_{H_2PO_4} - \beta_{HPO_4} + \beta_{Cl})^\circ$ is largely determined by the properties of the equimolal mixture of primary and secondary phosphates.[6] [7]

In view of these considerations, the last term of eq 4 is computed with the use of eq 5. The limiting value of the ion-size parameter, a°, is employed, and $(\beta_{H_2PO_4} - \beta_{HPO_4} + \beta_{Cl})^\circ$ is used for $\beta_{H_2PO_4} - \beta_{HPO_4}$. The equation for pH then becomes

$$pH = pK - \log \frac{m_{H_2PO_4}}{m_{HPO_4}} - \frac{3A\sqrt{\mu}}{1 + Ba^\circ\sqrt{\mu}} - (\beta_{H_2PO_4} - \beta_{HPO_4} + \beta_{Cl})^\circ \mu. \quad (4a)$$

The calculation of the pH of the buffer without sodium chloride thus rests upon the following assumptions:

1. The activity coefficients of the two phosphate anions and of chloride ion in a mixture containing all three ionic species are given as a function of total ionic strength by expressions of the Hückel type (eq 5). At a given temperature, each of these three ions has its characteristic a_i and β_i which remain unaltered with changing ionic strength. When the kinds or ratios of the ions in the mixture are changed, however, the value of β_i may change also, but a_i does not.

2. The limiting values of a^* and $(\beta_{H_2PO_4} - \beta_{HPO_4} + \beta_{Cl})$ as the ratio of the molality of sodium chloride to that of each phosphate salt approaches zero can be employed to compute $(f_{H_2PO_4}/f_{HPO_4})$ in equimolal phosphate buffers without added salt.

When eq 1 and 2 are combined, the following expression is obtained:

$$\frac{2A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} + \beta^*\mu = pK - \frac{E - E^\circ}{k} - \log \frac{m_{H_2PO_4}}{m_{HPO_4}} - \log m_{Cl}. \quad (7)$$

It is apparent that a^* and β^* can be obtained from two or more determinations of the right side of eq 7 for constant ratios of ions but changing ionic strength, provided pK is known. If the dissociation constant is to be evaluated, however, it is convenient to obtain these parameters from the extrapolation plots, as described in the previous section. Within the error of establishing a^*, the value of this parameter for all five series (m_{NaCl}/μ between 0.2 and 0.025), and hence also for the limit, was 4.4 Å at 25° C.

[6] These limiting values of the parameters actually describe the change of log $(f_{H_2PO_4} f_{Cl}/f_{HPO_4})$ with changing ionic strength when sodium chloride is absent. Use of the assumption that these parameters also describe the change of log $(f_{H_2PO_4}/f_{HPO_4})$ with ionic strength (when the appropriate alteration of the valence coefficient in the first term of the Hückel equation is made) implies that β_{Cl} is zero in the absence of sodium chloride but does not suggest that f_{Cl} is unity. Thus, at 25° C, f_{Cl} is 0.775 in an equimolal phosphate buffer of ionic strength 0.1 containing no sodium chloride.

[7] In earlier papers [1, 4, 23] it was assumed for the calculation of pH that $\beta_{HA} = \beta_A = \beta_{Cl} = \beta^*$. Although the effect of sodium chloride on mixtures of sodium phosphates has not been studied, a comparison of β^* for series A in the earlier article [1] with that for series A reported here indicates that the corrections to be subtracted from the pH values of 25° C of series A buffers studied in the earlier work are about 0.003, 0.007, and 0.013 at ionic strengths of 0.1, 0.2, and 0.4, respectively.

The experimental values of a^* and β^* are given in table 4. As mentioned above, a^* and $a°$ are identical. The table also lists the values of $3A$ and $Ba°$ [15] for convenience in the use of eq 4a.

TABLE 4.—*Parameters of the Hückel equation for phosphate buffers composed of equal molalities of potassium dihydrogen phosphate and disodium hydrogen, phosphate with and without sodium chloride.*

t	$a^*=a°$	$3A$	$Ba°$	β^* for series—					$(\beta_{H_2PO_4}-\beta_{HPO_4}+\beta_{Cl})°$
				A	B	C	D	E	
	A								
0	4.2	1.4649	1.3612	0.137	0.086	0.080	0.067	0.068	0.060
5	4.2	1.4763	1.3646	.143	.077	.076	.065	.062	.058
10	4.3	1.4880	1.4009	.131	.081	.076	.067	.066	.060
15	4.3	1.5000	1.4044	.119	.075	.072	.061	.058	.055
20	4.4	1.5126	1.4401	.128	.081	.076	.066	.063	.057
25	4.4	1.5255	1.4436	.102	.081	.075	.060	.059	054
30	4.4	1.5390	1.4476	.132	.079	.077	.061	.060	.053
35	4.4	1.5525	1.4507	.129	.080	.073	.065	.061	.056
40	4.5	1.5663	1.4873	.141	.094	.075	.070	.064	.058
45	4.5	1.5810	1.4913	.126	.083	.073	.072	.062	.057
50	4.5	1.5957	1.4945	.121	.081	.068	.070	.056	.055
55	4.6	1.6113	1.5313	.133	.088	.075	.070	.062	.058
60	4.6	1.6275	1.5355	.146	.083	.071	.071	.057	.057

As was found to be the case with phenolsulfonate buffers [4], the variation of β^* with the contribution of the sodium chloride to the ionic strength (m_{NaCl}/μ) was approximately linear. Since the pH is relatively insensitive to the limiting value of β^*, an adequate value of $(\beta_{H_2PO_4}-\beta_{HPO_4}+\beta_{Cl})°$ (within 0.005, which corresponds to 0.002 in the pH of the 0.1-*m* phosphate buffer) can readily be obtained. These extrapolated values are given in the last column of table 4. At temperatures other than 25° C, β^* for series A lies above the straight line drawn through the other four points. As figure 3 shows, however, the linear relationship is valid at 25° C.

Since the means of evaluating a^*, by choice of the function which yields the best straight line (see fig. 1), is incapable at these relatively low concentrations of furnishing values of this parameter that are more accurate than 0.1 to 0.2 A, a corresponding uncertainty is inherent in $a°$. It is thus important to consider what error in the pH is introduced by an error of 0.2 A in $a°$. At first this uncertainty appears to be a serious limitation to the accuracy of all pH values computed from eq 4a, for the term that contains $a°$ is 0.010 less at $a°=4.6$ than at $a°=4.4$, when the molality of each buffer salt is 0.1. It must be remembered, however, that a change in the value of a^* for any series would cause β^* also to be different.[8] The upper (dashed) line in figure 3 shows the changes of β^* when a^* for series A, B, C, D, and E is, respectively, 4.4, 4.5, 4.5, 4.6, and 4.6. The limiting values of a^* and β^* would then be 4.6 and 0.074 instead of 4.4 and 0.054, and the difference of pH would be 0.002 unit for the most concentrated buffer and correspondingly less for the more dilute ones.

[8] This interdependence of the two parameters of the Hückel equation has led to the formulation of single-parameter equations for activity coefficients. Van Rysselberghe and Eisenberg [24] express the $\beta\mu$ term as a function of a by considering it to be a measure of the van der Waals (or covolume) correction to the activity coefficient. Robinson and Harned [25] derived an empirical relation between a and β for 12 univalent electrolytes, finding β to be proportional to the fourteenth power of a. A critical discussion of these equations is given in the monograph of Harned and Owen [26].

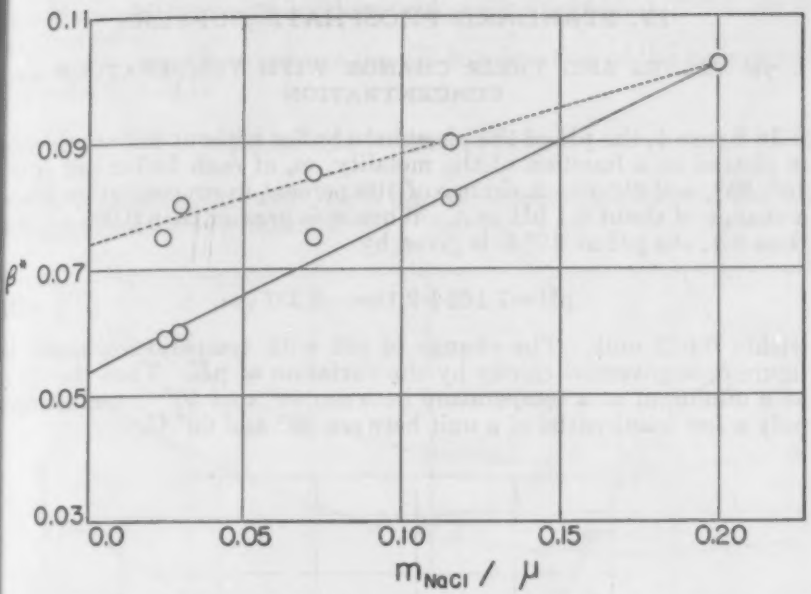

FIGURE 3.—*Plot of β* at 25° C as a function of the contribution of sodium chloride to the ionic strength.*

Table 4 shows that $(\beta_{H_2PO_4}-\beta_{HPO_4}+\beta_{Cl})°$ is practically the same for all 13 temperatures. The mean value is 0.057 ± 0.002. Inasmuch as the maximum departure from the mean is 0.004 at 30° C, or 0.0016 in the pH of the most concentrated buffer, the mean value was employed in eq 4a for the calculation of the pH at all temperatures. The pH values of phosphate buffers composed of equal molal quantities of potassium dihydrogen phosphate and disodium hydrogen phosphate without sodium chloride are given in table 5. The average values of pK given in the last column of table 2 were used. It is estimated that the pH has a precision of ±0.003.

TABLE 5.—pH *of equimolal phosphate buffers without sodium chloride*

t	pH for buffer of molality—							
	0.005	0.01	0.02	0.025	0.04	0.05	0.075	0.1
°C								
0	7.138	7.081	7.012	6.983	6.925	6.895	6.836	6.792
5	7.106	7.048	6.976	6.950	6.891	6.861	6.802	6.758
10	7.077	7.019	6.948	6.922	6.864	6.832	6.776	6.732
15	7.053	6.995	6.922	6.896	6.838	6.808	6.750	6.706
20	7.034	6.976	6.904	6.878	6.820	6.791	6.733	6.690
25	7.018	6.959	6.886	6.860	6.802	6.772	6.714	6.671
30	7.007	6.948	6.875	6.849	6.790	6.760	6.702	6.658
35	7.001	6.942	6.868	6.842	6.782	6.752	6.694	6.650
40	6.996	6.937	6.863	6.837	6.778	6.748	6.690	6.647
45	6.994	6.934	6.860	6.834	6.775	6.745	6.686	6.642
50	6.995	6.934	6.859	6.833	6.773	6.743	6.684	6.640
55	6.997	6.935	6.862	6.836	6.777	6.747	6.688	6.645
60	7.002	6.941	6.866	6.840	6.780	6.749	6.691	6.647

IV. STANDARD PHOSPHATE BUFFERS

1. pH VALUES AND THEIR CHANGE WITH TEMPERATURE AND CONCENTRATION

In figure 4, the pH of the phosphate buffer without sodium chloride is plotted as a function of the molality, m, of each buffer salt at 0°, 10°, 25°, and 60° C. A change of 100 percent in concentration effects a change of about 0.1 pH unit. When m is greater than 0.005 and less than 0.1, the pH at 25° C is given by

$$\mathrm{pH}=7.162+2.18m-2.237\sqrt{m}, \tag{8}$$

within 0.002 unit. The change of pH with temperature, shown in figure 5, is governed chiefly by the variation of pK. Thus the pH is at a minimum at a temperature between 40° and 50° C and changes only a few hundredths of a unit between 20° and 60° C.

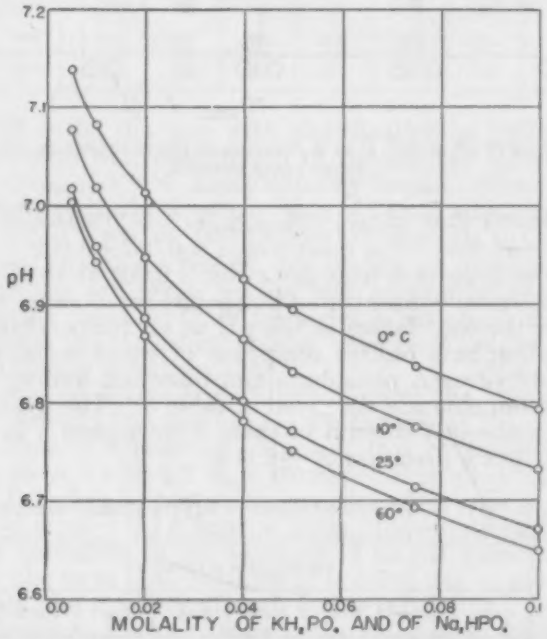

FIGURE 4.—pH *of phosphate buffers as a function of molality at 0°, 10°, 25° and 60° C*

The densities of four phosphate buffers, of molalities 0.01, 0.02, 0.05, and 0.1, were determined at 25° ±0.01° C with a picnometer that had a volume of approximately 57 ml. The results are given by the equation

$$c/m=0.99707-0.0477m-0.024m^2, \tag{9}$$

where c represents the concentration of each buffer salt expressed in moles per liter of solution. The mean departure of the values of c/m calculated by this equation from those computed from the measured

densities is ±0.00001, or 0.001 percent. The upper limit of validity of eq 9 is $m=0.1$.

It is now possible to express the pH as a function of the molarity of the buffer [9] by eq 10

$$\mathrm{pH}=7.169+2.39c-2.324\sqrt{c}. \tag{10}$$

In the concentration range 0.005 c to 0.1 c, eq 10 reproduces the pH with an accuracy of 0.002 unit.[10]

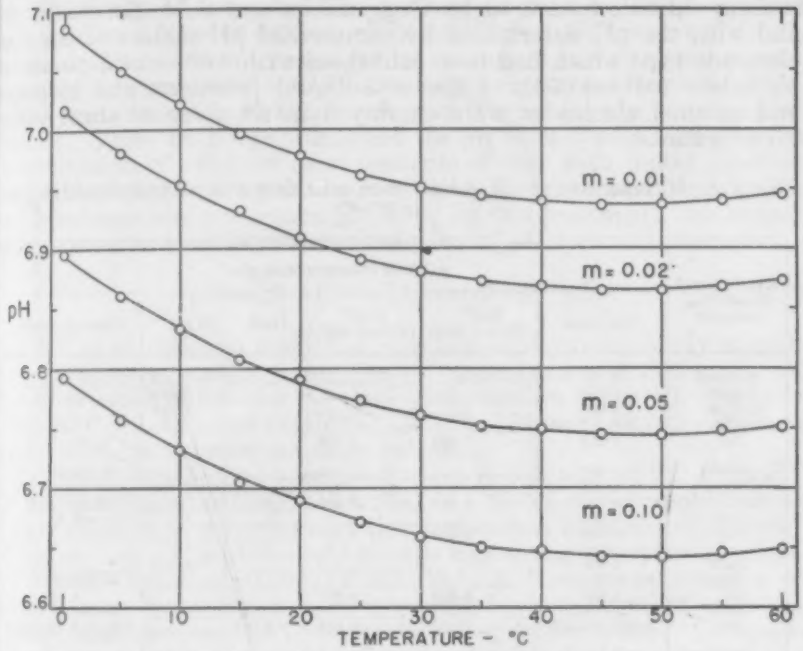

FIGURE 5.—pH *of four phosphate buffers as a function of temperature.*

By differentiation of eq 10, one obtains

$$\mathrm{d(pH)}/dc=2.39-1.162/\sqrt{c}, \tag{11}$$

from which the change of pH that accompanies small changes in c can be computed. With the use of eq 9, the difference, dc, in molar concentration between buffer solutions which are, respectively, s molal and x molar in each salt can be found. From eq 11 it can be shown that the pH of a 0.01-molar phosphate buffer differs from that of a 0.01-molal buffer by only 0.0003 unit, whereas the difference

[9] The pH given by eq 10 is referred to the same standard state as that used throughout this paper: $\mathrm{pH}=-\log a_H$, where a_H is the activity of hydrogen ion on the molal or weight basis. Since the infinitely dilute solution is normally chosen as the standard state on both the molal (m) and molar (c) scales, $a_c=a_m d^\circ$, where d° is the density of the solvent. Hence, the pH is the same at 4° C on the molar and molal scales and differs at 25° and 60° C by 0.0013 and 0.0073 unit, respectively.

[10] Obviously, eq 8 and 10 are merely formalized representations of the pH in the range of molalities (and molarities) between 0.005 and 0.1, for unlimited dilution of the buffer must yield the pH of pure water. Since the pH is rather close to neutrality, the buffer effect will persist to fairly low concentrations. On the other hand, a solution of which the pH is far removed from neutrality will begin to lose its regulating power at relatively high concentrations.

is 0.0010 unit when the buffers are 0.1 molar and 0.1 molal. Since this larger difference is within the limits of accuracy assigned to the pH in table 5, the pH of a buffer the molar concentration of which is known can be considered the same as that of the solution of numerically equal molality.

The pH values at 25° C of the phosphate buffer derived from measurements of cells without liquid junction are compared in table 6 with the pH of five buffers studied by Hitchcock and Taylor (H&T) [8], with six measured by Michaelis and Krüger (M&K) [27], with those of three buffers composed of sodium phosphates and sodium chloride measured by Guggenheim and Schindler (G&S) [7], and with the pH determined by commercial pH meters of the glass electrode type which had been calibrated with 0.05-*m* acid potassium phthalate (pH=4.005). Cells with liquid junctions and hydrogen and calomel electrodes were employed in all three of these earlier investigations.

TABLE 6.—*Comparison of* pH *derived from cells with and without liquid junction at 25° C*

KH_2PO_4 and Na_2HPO_4, molarity	pH from measurements of—					
	This paper	H&T ($E^{\circ\prime}$=0.2442)	H&T ($E^{\circ\prime}$=0.2447)	G&S	M&K [a]	Glass electrodes
0.000665	7.111				7.102	
.00133	7.087				7.082	
.00167	7.078				7.083	
.0025	7.064; [b] 7.050			[c] 7.072		[d] 7.06
.005	7.018	7.024	7.016			7.01 to 7.02
.00625	7.001					[d] 7.00
.00667	6.993				7.004	
.01	6.959	6.961	6.953			6.94 to 6.96
.0125	6.938					[d] 6.93
.015	6.919	6.919	6.911			
.01667	6.909				6.918	
.01875	6.895					[d] 6.89
.02	6.886	6.885	6.877			6.87
.0225	6.874					[d] 6.86
.025	6.860; [b] 6.833	6.857	6.848	[c] 6.837		6.85 to 6.86; [d] 6.86
.03333	6.825				[e] 6.827	
.04	6.802					6.79
.05	6.772; [b] 6.741			[c] 6.735		6.76 to 6.78
.1	6.671					6.66 to 6.69

[a] Recalculated with the use of 0.3358 v for the potential of the *N*/10 calomel electrode at 18° C; the pH at 25° C was obtained by subtracting 0.024 unit from the pH at 18° C.
[b] pH of the buffer that contains sodium chloride equal in concentration to that of each phosphate.
[c] Buffers prepared with sodium dihydrogen phosphate instead of the corresponding potassium salt. Sodium chloride in concentration equal to that of each phosphate.
[d] Measurement of Glaubiger [29] with the Young "Electron-Ray" pH meter.
[e] Measurement of Sørensen [28] leads to the same value for this buffer.

The solutions studied by Guggenheim and Schindler are not strictly comparable with the others listed in the table, for they contained sodium chloride and the primary sodium salt. The results for these solutions have been included, however, in recognition of the fact that this substitution of the sodium salt for the potassium salt may not introduce an uncertainty any greater than that involved in the estimation of the potential at the liquid boundary. Cohn [6] has reexamined the data obtained by Sørensen [28] and Michaelis and Krüger at 18° C. We have made a further adjustment of these values to conform to a

potential of 0.3358 for the $N/10$-calomel electrode at 18° C and have obtained the pH at 25° C by subtracting 0.024 unit from the pH at 18° C.

The agreement of the results of this investigation with all three sets of earlier values is quite satisfactory. The pH measurements with the glass electrode agree with the computed pH within the limits of accuracy of the commercial instruments [30, 34]. The measurements of Glaubiger [29] show agreement of a higher order than can normally be expected of a cell with glass electrode and a liquid junction. His results are, on the average, 0.006 unit lower than those given in the second column of table 6. The instrument used by Glaubiger was calibrated at 4.00 with 0.05-*m* phthalate buffer. If a value of 4.005, 4.008, or 4.01 had been chosen for this standard, as is usually recommended, the agreement would have been even more complete.

The measurements of Hitchcock and Taylor [8] are of particular interest. These authors approached the problem of standardizing the determination of pH from measurements of cells with liquid junction in a manner suggested by the work of Cohn, Heyroth, and Menkin [31] and MacInnes and coworkers [32, 33]. In this treatment, the simple emf equation is used for the computation of pH,

$$\mathrm{pH}=(E-E^\circ-E_j)/k=(E-E^{\circ\prime})/k, \qquad (12)$$

and $E^{\circ\prime}$ is adjusted to make the equation conform as closely as possible to thermodynamic quantities. Guggenheim and Schindler, on the other hand, computed E_j, the liquid-junction potential, from the Henderson equation and employed a selected value of E°, the standard potential of the calomel reference half-cell.

Hitchcock and Taylor assigned a value of 0.2442 v at 25° C to $E^{\circ\prime}$ for their saturated calomel electrode, as a result of extrapolations to infinite dilution of a function of the dissociation constant of primary phosphate ion [19] and the emf of cells containing phosphate buffers. An average value of 0.2441 v was chosen from measurements of acetate, phosphate, borate, and glycolate buffers, together with the dissociation constants of the corresponding buffer acids. Comparison of the second and third columns of table 6 demonstrates the essential agreement between the Hitchcock and Taylor pH scale and that defined by our method which utilizes measurements of cells without liquid junction.

In order that the results of the two investigations might relate to the same value of the dissociation constant, the measurements made with phosphate buffers by Hitchcock and Taylor at 25° and 38° C have been recalculated with the use of the Hückel equation and with pK and a° listed in this paper. The extrapolation plot was a straight line of small slope for each temperature. At 25° C, $E^{\circ\prime}$ from the measurements with phosphate buffers becomes 0.2447 v. If this value is used in eq 12, the pH of each solution measured by Hitchcock and Taylor is lowered by 0.008 unit, as shown in the fourth column. MacInnes, Belcher, and Shedlovsky [33], from extrapolation of their measurements of cells containing acetate and chloroacetate buffers, concluded that $E^\circ+E_j$ has a value of 0.2446 v at infinite

dilution.[11] The emf data of Hitchcock and Taylor at 38° C were obtained from measurements of the cell, H_2|Buffer‖KCl (saturated) ‖HCl (0.1 *c*)|H_2, for which they chose $E°+E_j=-0.0668$ v. Recalculation with $pK=7.182$ yields -0.0666 v for $E+E_j$ at 38° C. The two sets of pH values are given in table 7. The last column gives data obtained by Glaubiger (G) [29] with the glass electrode.

TABLE 7.—*Comparison of* pH *derived from cells with and without liquid junction at 38° C*

KH_2PO_4 and Na_2HPO_4, molarity	pH from measurements of—			
	This paper	H&T ($E°'=-0.0668$)	H&T ($E°'=-0.0666$)	Glass electrodes (G)
0.0025	7.045	7.048	7.045	7.03
.00625	6.981	6.983	6.980	6.97
.0125	6.917	6.918	6.915	6.90
.01875	6.874	6.871	6.868	6.86
.0225	6.854	----------	----------	6.83
.025	6.840	6.837	6.834	6.83

The mean differences between the pH at 25° C obtained by Hitchcock and Taylor from measurements of cells with liquid junction and the pH derived here from measurements of cells without liquid junction are only 0.002 unit ($E°'=0.2442$) and 0.005 unit ($E°'=0.2447$). At 38° C, the differences are 0.002 unit ($E°'=-0.0668$) and 0.003 unit ($E°'=-0.0666$).

When the pH values are made to conform to the same thermodynamic constant, complete agreement is found for the dilute buffers on the two scales. The pH on the scale of Hitchcock and Taylor falls farther below the values reported in this paper as the ionic strength increases. For a fivefold increase in concentration of the buffer, the values of Hitchcock and Taylor and of Michaelis and Krüger both exhibit a decrease of 0.009 unit relative to the pH given in the second column. It is, perhaps, not surprising to discover that the potential at the liquid junction does not remain constant with changing concentration of the buffer, as is assumed in their method. With the values of this article as a reference, a difference of 0.6 mv between E_j for phosphate buffers of 0.005- and 0.025-molar concentration is computed from eq 12. In this manner $E°+E_j$ at 25° C can be found for each of the phosphate buffers. To reproduce the pH values of table 5, $E°+E_j$ for the saturated calomel electrode used by Hitchcock and Taylor must change with concentration of buffer. The potentials for buffers of molar concentrations 0.005, 0.01, 0.015, 0.02, and 0.025 would be, respectively, 0.2446, 0.2443, 0.2442, 0.2442, and 0.2440 v. Although such a change is to be expected, it cannot be stated definitely that the error does not reside in the method of computing pH from measurements of cells without liquid junction.

[11] A value of 0.2434 v for $E°+E_j$ at ionic strengths of 0.04, 0.07, and 0.1 was found by Manov, DeLollis, and Acree [34] from measurements at 25° C of hydrogen-calomel cells with liquid junctions. Their calculation was made, with the use of eq 12, from the pH values and emf obtained in this Bureau for phthalate, phosphate, phenolsulfonate, and borate buffers and a mixture of hydrochloric acid and sodium chloride, from all of which oxygen was rigorously excluded. In the presence of air 0.2446 v was obtained for $E°+E_j$. It must be remembered that intercomparison of the values of $E°+E_j$ obtained by various investigators is not always justifiable, for this quantity is dependent not only upon the kinds and concentrations of ions at the boundary but upon the manner of forming the junction as well.

The measurements of Glaubiger [29], on the other hand, do not reveal a similar change of liquid-junction potential with a change in the concentration of equimolal phosphate buffer. The agreement of his results with the pH reported here leads to the conclusion that the potential at the liquid junction between saturated potassium chloride and 0.05-*m* phthalate buffer does not differ greatly from that at the boundary between saturated potassium chloride and phosphate buffers of concentrations that range from 0.0025 *m* to 0.025 *m*. Since the total change in potential is not much greater than the precision of Glaubiger's measurement, this discrepancy need cause little concern.

2. PREPARATION OF PHOSPHATE BUFFERS

These buffers are best prepared from freshly boiled distilled water and weighed amounts of each anhydrous salt, or of a carefully prepared mixture of the solid phosphates. The compositions of eight useful buffer solutions are given in table 8. Inasmuch as anhydrous disodium hydrogen phosphate will take up moisture when the relative humidity exceeds about 41 percent at 25° C, it is considered good practice always to dry this salt, or the mixture of solid salts, at 110° to 130° C for at least 2 hours.

TABLE 8.—*Compositions of standard phosphate buffers*

Moles of each phosphate per liter of solution	pH	KH_2PO_4	Na_2HPO_4	Equimolal mixture of buffer salts
	(25° C)	g/liter	g/liter	g/liter
0.005	7.018	0.6805	0.7099	1.390
.01	6.959	1.361	1.420	2.781
.02	6.886	2.722	2.840	5.562
.025	6.860	3.402	3.550	6.952
.04	6.802	5.444	5.680	11.12
.05	6.772	6.805	7.099	13.90
.075	6.714	10.21	10.65	20.86
.1	6.671	13.61	14.20	27.81

It is evident from a consideration of the properties of a buffer composed of two salts that departures of the buffer ratio from unity will cause larger errors in the pH of the buffer than will inaccuracies in total composition. If the ratio, moles KH_2PO_4/ moles Na_2HPO_4, is between 0.996 and 1.004, however, the pH will not differ by more than 0.002 unit from that calculated for equal molal quantities of the two salts. It is well to strive for an accuracy of 0.1 percent in the weight of each salt used in the preparation of a standard phosphate buffer. The total volume of the buffer should be correct within 8 ml/ liter, or 0.8 percent, if an accuracy in composition corresponding to 0.001 pH unit is desired.

Inasmuch as all of these standard buffers are prepared from equal molal amounts of the two phosphates, it would be a convenience to the user to have at hand a mixture of the pure anhydrous salts in the proper proportions. An experiment was therefore performed to ascertain whether such a mixture of solid salts would be mechanically stable in shipment and storage.

One bottle, half filled with a powdered mixture of the two salts in equal molal proportions, and one full bottle of the same mixture, were

shipped by mail twice from Washington, D. C., to San Diego, Calif., and back to Washington. Five buffer solutions, each 0.02 *m* in sodium chloride and 0.02 *m* with respect to both primary and secondary phosphate salts if segregation had not occurred, were prepared with the use of the top 4 g of salt mixture in each of these two bottles and three controls. Eight cells with hydrogen electrodes and silver–silver-chloride electrodes were prepared from these solutions and emf measurements made at 25° C. The average emf, corrected to a pressure of hydrogen of 760 mm, was 0.73473 v, and the average deviation was 0.03 mv. Inasmuch as the emf of this cell was found to be 0.73478 v from a plot of the data given earlier in this paper, it was concluded that little or no segregation had taken place. The possibility that prolonged exposure to the normal vibrations of the laboratory shelf might effect appreciable segregation cannot, however, be ignored.

V. EFFECT OF SODIUM CHLORIDE ON THE pH

The pH of an equimolal phosphate buffer containing sodium chloride cannot be calculated from measurements of cells of the type used in this work and the two assumptions made earlier in this paper. In order to do so, it would be necessary to evaluate $\beta_{H_2PO_4^-} - \beta_{HPO_4^=}$ in the presence of the chloride. The decrease of β^* as the molality of sodium chloride is lowered at constant ionic strength (see fig. 3) is partitioned in an unknown manner among the values of β for the three ions concerned. Whereas it was assumed that $\beta_{H_2PO_4^-} - \beta_{HPO_4^=}$ in the absence of chloride can be identified with the limiting value of β^*, this term must logically be considered, in the light of the first assumption made earlier, to change when sodium chloride is added to the buffer solution. If this were not the case, there would be no "specific salt effect," and the pH of a buffer solution with salt and one without salt could both be calculated from eq 4a without a change in the ionic parameters.

In an unpublished investigation of the effect of neutral salts of different valence types upon the pH of the equimolal phenolsulfonate buffer, the authors of this paper concluded that potassium nitrate, sodium sulfate, and trisodium citrate displayed only slight specific effects in their influence upon the pH. As a first approximation, each salt lowered the pH by the same amount as did an equimolal mixture of the buffer salts which contributed the same amount to the ionic strength. In view of the fact that a knowledge of the approximate pH of phosphate buffers with added sodium chloride is often desired, such a calculation has been made on the assumption that the influence of sodium chloride is, in this instance also, a "normal salt effect." It seems improbable, by analogy with the equimolal phenolsulfonate buffer, that this assumption should introduce an error greater than 0.005 unit when the ionic strength is 0.5 and the molalities of sodium chloride and of buffer are equal.

If equations of the form of eq 4a are written for the pH of a 1:1 phosphate buffer with no chloride at the ionic strength μ, and for the pH of the same buffer, pH′, to which sodium chloride has been added to a molality m_2, an expression is obtained, by the subtraction of one equation from the other, for pH′ in terms of the pH of the buffer without chloride:

$$pH' = pH - \frac{3A\sqrt{\mu + m_2}}{1 + Ba^\circ\sqrt{\mu + m_2}} + \frac{3A\sqrt{\mu}}{1 + Ba^\circ\sqrt{\mu}} - (\beta_{H_2PO_4} - \beta_{HPO_4} + \beta_{Cl})^\circ m_2, \quad (13)$$

or

$$pH' = pH - \phi(m_2). \quad (13a)$$

Within 0.002 pH unit, $\phi(m_2)$ is given empirically by

$$\phi(m_2) = (1 + at)(bm_2 + cm_2^2) \quad (14)$$

for temperatures, t, between 0° and 60° C.

The constants of eq 14 were determined by the method of least squares and lead to the following expressions for the effect of sodium chloride on eight phosphate buffers, each of which contain equal molal concentrations (m) of potassium dihydrogen phosphate and of disodium hydrogen phosphate:

0.005-m buffer: $pH' = pH - (1 + 0.0009t)(3.06m_2 - 13.2m_2^2)$. (15a)
0.01-m buffer: $pH' = pH - (1 + 0.0006t)(2.13m_2 - 7.6m_2^2)$. (15b)
0.02-m buffer: $pH' = pH - (1 + 0.0004t)(1.36m_2 - 3.6m_2^2)$. (15c)
0.025-m buffer: $pH' = pH - (1 + 0.0003t)(1.16m_2 - 2.8m_2^2)$. (15d)
0.04-m buffer: $pH' = pH - 0.84m_2 + 1.6m_2^2$. (15e)
0.05-m buffer: $pH' = pH - 0.66m_2 + 0.8m_2^2$. (15f)
0.075-m buffer: $pH' = pH - 0.48m_2 + 0.4m_2^2$. (15g)
0.1-m buffer: $pH' = pH - 0.40m_2 + 0.4m_2^2$. (15h)

The pH value of each buffer without sodium chloride at each of 13 temperatures appears in table 5. These equations apply strictly only when the molality of sodium chloride (m_2) is equal to, or less than, the molality, m, of each buffer salt.

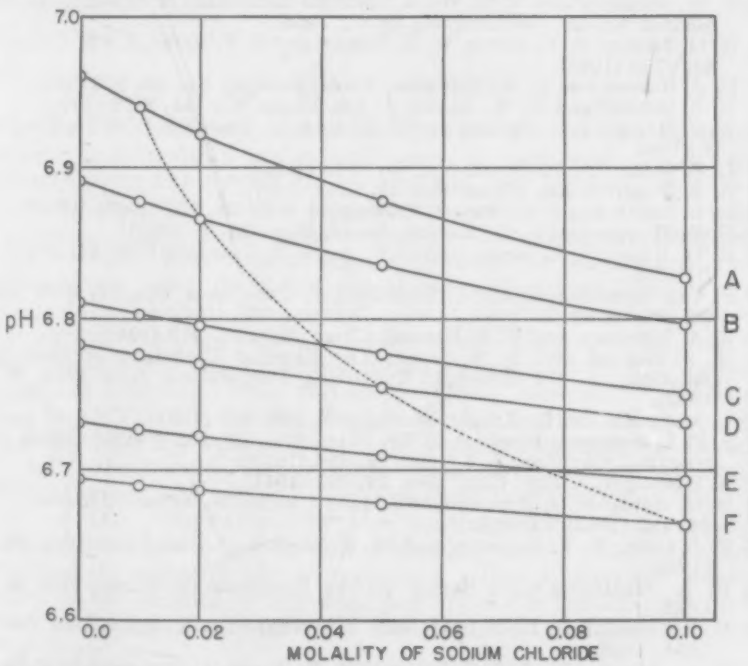

FIGURE 6.—*Effect of sodium chloride on the* pH *of six phosphate buffers.*

Curves *A*, *B*, *C*, *D*, *E*, and *F* represent buffers in which both phosphates are respectively 0.01, 0.02, 0.04, 0.05, 0.075, and 0.1 molal.

In figure 6, the pH of six of these buffers is plotted as a function of molality of added sodium chloride for values of m_2 up to 0.1. The dashed line which intersects all of the curves separates that portion of each curve (on the left) which lies in the range of concentrations of the experimental measurements from that portion (on the right) which was computed from 15a to 15h beyond the region of their validity.

The authors are indebted to C. G. Malmberg for distilling the conductivity water used in the preparation of the solutions and for measuring its conductance.

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[31] E. J. Cohn, F. F. Heyroth, and M. F. Menkin, J. Am. Chem. Soc. **50,** 696 (1928).
[32] D. A. MacInnes, Cold Spring Harbor Symposia on Quant. Biol. **1,** 190 (1933).
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U. S. Department of Commerce National Bureau of Standards

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MELTING POINT OF ALPHA-ALUMINA

By R. F. Geller and P. J. Yavorsky

ABSTRACT

Results are given of seven melting-point determinations on alpha-alumina of high purity in an oxidizing atmosphere and under atmospheric pressure. There was detectable contamination of the specimens by vapors of other elements in the furnace atmosphere, but the results are believed to show that the melting point of alpha-alumina is within the range 2,000° to 2,030° C.

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I. INTRODUCTION

In the determination of a value for the temperature at which an element or compound melts, or freezes, the value obtained depends not only upon the purity of the material, the method, and the skill employed, but also on the temperature scale on which the value is expressed. Prior to the adoption of the International Temperature Scale [1] in 1927, there was no scale in general use, particularly for high temperatures, and in many cases the differences between values reported for the same temperature are attributable at least in part to differences in the temperature scales used. Consequently, one must take into account the scale used by an investigator when his reported values are compared with values previously reported. This is especially important for values determined prior to 1927. In some cases, sufficient data are available to permit expressing such values on the present International Temperature Scale, but in others the available information, or the method used, does not make this possible.

In all the observations of the melting point of alpha-alumina (Al_2O_3) that have come to our attention, an optical pyrometer was employed to measure the temperature. The pyrometers were calibrated at the melting, or freezing, point of one or more metals (or compared with an optical pyrometer that had been so calibrated) and an

[1] George K. Burgess, BS J. Research 1, 635 (1928) RP22.

equation of some form applied for extrapolating to the melting point of Al_2O_3. The different melting, or freezing, points at which the pyrometers were calibrated, the different values assigned to these points, and the equations used for extrapolating, constitute the differences in the temperature scales referred to above.

For any given sample of alumina, the temperature at which it melts will depend not only upon the initial purity but also upon the kind and amount of impurity "picked up" from the furnace atmosphere and the specimen support. In most of the previous reports on the melting point of alumina, some reference was made to the initial purity, but no attempt was made after the test to determine the purity at the time the specimen melted.

II. PREVIOUS DETERMINATIONS

The value usually given in the literature for the melting point of alpha-Al_2O_3 is 2,050° C as determined by Kanolt,[2] who calibrated his optical pyrometer at the melting points of antimony, silver, copper, and diopside. As a check on his pyrometric apparatus as a whole, he determined the melting point of platinum, to which he assigned the value 1,755° C. However, he did not heat the platinum by the same method or in the same furnace as he did the Al_2O_3. Consequently, any correction of his reported values to the International Temperature Scale would be spurious.

Three years earlier, Ruff and Goecke [3] had reported the value 2,020° C for the melting point of Al_2O_3. This was determined in a graphite resistance furnace and in nitrogen under atmospheric pressure, but the purity of the specimens, which rested on Al_2O_3, was not indicated. Their optical pyrometers, of which they used one for viewing the specimen through the side of the furnace and the other from the top, were calibrated by observing the melting of gold and of platinum in the same furnace. In their calculations they used 1,071° C for the melting point of gold and 1,757° C for platinum. When the Al_2O_3 was heated under reduced pressure (6 mm Hg), they noted lively vaporization at 1,740° C.

In 1916 Ruff and Lauschke,[4] also using a graphite resistance furnace and reduced pressure (7.5 and 7.7 mm Hg), reported observing the melting of Al_2O_3 at 2,008° C and 2,005° C, respectively. Their optical-pyrometer calibration was based on the melting point of gold with an assigned value of 1,062.4° C, and on 1.437 cm-degrees centigrade for the constant C_2 in Wien's formula.[5] These melting-point values for Al_2O_3 correspond to about 2,020° C and 2,017° C, respectively, when recalculated on the basis of 1,063°C for the gold point and 1.432 for C_2. The Al_2O_3 was described as a white powder with an ignition loss of 3.5 percent, indicating that it was prepared from a salt and that it was probably of high purity. Their heating rates were 48 and 67 degrees centigrade a minute.

In 1931 Weigel and Kaysser,[6] published the results of what appears to have been a carefully conducted series of melting-point determinations, but here again the purity of the Al_2O_3 was only implied. Their

[2] C. W. Kanolt, Bul. BS **10**, 295 (1914) S212.
[3] Otto Ruff and Otto Goecke, Z. angew. Chem. **242**, 1459 (1911).
[4] Otto Ruff and George Lauschke, Z., anorg. allgem. Chem. **97**, 73 (1916).
[5] H. T. Wensel, J. Applied Phys. **11**, 373 (1940).
[6] O. Weigel and F. Kaysser, Neues Jahrb. Mineral. Geol. Beil. **64** [A], 321 (1931).

synthetic corundum was a massive crystalline material furnished by I. G. Farbenindustrie, and the powdered samples were described as the purest Kahlbaum preparations of Al_2O_3 for reagent purposes, and of alkali-free hydroxide. The furnace was of the graphite resistance type, with a ZrO_2 inner lining through which either N_2, or air, could be passed as desired. The calibration of the optical pyrometer was based on 1,063° C for the melting point of gold and on the value 1.430 for the constant C_2. The calibration and melting-point technic was checked by observing the melting of silver, gold, palladium, platinum, rhodium, and iridium. Of immediate interest is their accepted value of 1,770° C for platinum, which is in good agreement with the value of 1,773.5° C for this point on the International Temperature Scale.

In 34 tests, specimens of the corundum were fused on charcoal in a nitrogen atmosphere, and at a heating rate which ranged from 5 to 20 degrees centigrade a minute. The melting-point values ranged from 1,990° to 2,037° C, with a mean of 2,007° ±4° C. For a single determination with the specimen on iridium and in a stream of air, melting was observed at 2,001° C; the tested specimen was described as water clear. The average of 40 tests on the powders was 2,001° ±4° C, using charcoal as the support for the specimens (which had been formed by pressing, with gum tragacanth as the binder) and an atmosphere of nitrogen. No difference in results was noted for the oxide and the hydroxide. Weigel and Kaysser also determined the melting point of the Al_2O_3 powder in air and on iridium. For these tests, a small piece of rhodium wire was placed upon the alumina specimen and in two trials the Al_2O_3 was observed to melt 35 and 40 degrees centigrade respectively, above the melting temperature for the rhodium. Accepting 1,966° [7] as the melting point of rhodium on the International Temperature Scale places the melting of the alumina at 2,001° C in the first test and at 2,006° C in the second. If the weighted average of all of their values is recalculated to the International Temperature Scale, we obtain 2,000° C.

Weigel and Kaysser also conducted several tests with colorless natural sapphire from Ceylon and with bluish and greenish natural corundum from Australia. It is interesting that they obtained higher values for these specimens—2,022° ±9° C for the former and 2,021° ±4° C for the latter.

Bunting [8] reported the melting of Al_2O_3 at 2,040° C and at 2,045° C. His optical pyrometer was calibrated at the National Bureau of Standards, and his values are expressed on the international scale. The oxide was prepared by dissolving aluminum of 99.95 percent purity in reagent quality HNO_3, and igniting at 1,400° C. All reactions were carried out in platinum. The granules of sintered alumina were placed in a well (about 7 mm deep by 4 mm in diameter) formed in the top of an iridium pellet, which was then heated by induction in air and under atmospheric pressure. The temperature was raised quickly to about 2,000° C and then increased at 5 to 10 degrees centigrade a minute, until the specimen of Al_2O_3 was seen to melt. The pyrometer was sighted on the iridium.

[7] Wm. F. Roeser and H. T. Wensel, BS J. Research **12**, 519 (1934) RP676.
[8] E. N. Bunting, BS J. Research **5**, 325 (1930) RP203; **6**, 947 (1931) RP317.

In 1943 Geller and Bunting [9] reported the value 2,035° C for the melting point of Al_2O_3. They used the same pyrometer previously used by Bunting (see footnote 8), but fragments of the Al_2O_3 were placed upon iridium (fig. 1), the pyrometer was sighted directly on the specimen, and the furnace was heated with ThO_2-CeO_2 resistors.[10] This value of 2,035° C represented seven determinations ranging from 2,000° to 2,040° C, and the alumina was believed to be at least 99.9 percent pure.

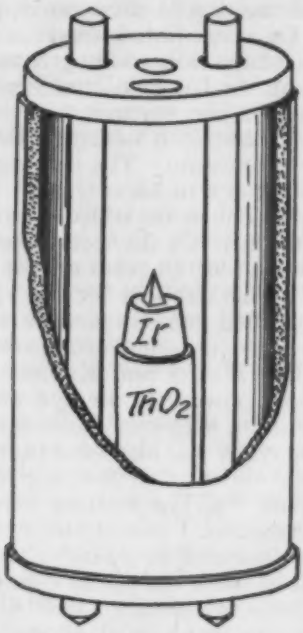

FIGURE 1.—*Furnace setup for melting-point tests.*

Cut-away section of the heating chamber in the furnace described in J. Research NBS 27, 555 (1941) RP1443. The chamber was made of thoria, and the resistors, of which two are shown in place, were made of 85 percent thoria and 15 percent ceria. The pyramidal-shaped specimen rests on an iridium "button," which is supported by a thoria pedestal.

Because of several factors which, at the time, were not recognized as militating against the accuracy of the results, the authors feel that the value of 2,035° C is to be questioned.

As a part of further high-temperature investigations, seven additional determinations were made under conditions considered to be productive of more reliable data, and the results are reported in this paper.

III. MATERIALS

Alumina from three sources was used:

Alumina A.—This had been fused and recrystallized by the Norton Co., Worcester, Mass. The sample was submitted by Raymond R. Ridgway, who described it as soda free and containing 0.05 percent

[9] R. F. Geller and E. N. Bunting, J. Research NBS 31, 255 (1943) RP1564.
[10] R. F. Geller, J. Research NBS 27, 555 (1941) RP1443.

of included carbon, the balance being Al_2O_3. The specimens were irregular fragments of crystals about 3/16 in. in maximum dimension.

Alumina B.—This was obtained from another industrial concern. The specimens were formed by cutting them to the desired shape with a diamond impregnated wheel from a single crystal of synthetic colorless corundum about 1/8 in. in diameter. Spectrographic analysis indicated that it contained about 99.99 percent of Al_2O_3, and that the 0.01 percent of impurity was about four-tenths CaO and about three-tenths SiO_2.

Alumina C.—This was prepared by dissolving aluminum of 99.987 percent purity [11] with reagent quality HNO_3 and igniting at 1,100° C. All reactions were carried out in platinum, and the spectrogram of the sintered oxide indicated less than 0.01 percent each of Ag, B, Ca, Cu, Fe, Mg, and Si. The specimens, about 3/16 in. in maximum dimension, were irregular fragments of this sintered and porous sample.

IV. TEMPERATURE MEASUREMENTS

Three Leeds & Northrup optical pyrometers were used, and all were calibrated at the National Bureau of Standards. They indicated temperatures on the international scale, based on 1,063° C as the gold point and 1.432 cm-degrees for the constant C_2 in the following formula, as presented and discussed by Wensel.[12]

$$\frac{1}{t+273}=\frac{1}{t_0+273}-\frac{\lambda \ln (J/J_0)}{C_2},$$

in which

t=determined temperature, °C.
t_0=gold point (1,063°).
J=radiant energy of wavelength, λ, from black body at temperature t.
J_0=the corresponding value for temperature t_0.
ln=natural logarithm.

Pyrometer D.—This was the same instrument used by Bunting (see footnote 8), and later by Geller and Bunting (see footnote 9), except that it had been reconditioned and recalibrated.

Pyrometer E.—This was of recent manufacture, permitting a clearer image of the specimen and more precise tempertature readings than was possible with pyrometer *D*.

Pyrometer F.—This was a new instrument of the same model as pyrometer *E*.

V. METHOD

The specimens were heated in air, under atmospheric pressure, and on iridium, using the furnace described by Geller (see footnote 10) and the arrangement shown in figure 1. By careful placement of the iridium "button" so that its flat (or slightly concave) upper surface was perpendicular to the line of vision, an effect was obtained in which the flat iridium surface reflected less light to the pyrometer than did the specimen. As a result, the metal appeared slightly colder than the specimen and made it visible in outline.

[11] James I. Hoffman and G. E. F. Lundell, J. Research NBS **19**, 1 (1937) RP967.
[12] H. T. Wensel, J. Am. Ceram. Soc. **19**, 81 (1936).

By using specimens which showed sharp corners in outline, as viewed from above, the beginning of melting could be observed as a dulling, or rounding, of the corners, and the corresponding temperature was obtained by sighting the pyrometer on the specimen.

In order to check the accuracy of the temperature measurements, each pyrometer was used to observe the melting of platinum or of a platinum-rhodium alloy. These observations were made in the same furnace by using pieces of wire which rested on a refractory oxide base in place of the iridium. In this case, the wire could be seen because its surface reflected the colder observation hole and also the slightly hotter heating elements. The pyrometer was sighted on the refractory, for which ThO_2, ZrO_2, or Al_2O_3 was used. The observations show that black-body conditions were realized and that the over-all inaccuracies of the temperature measurements were within the limits of the optical pyrometer, which was certified to ± 10 degrees centigrade. The actual values obtained are as follows:

60 Pt-40 Rh	1,925°C	Published value [13]	1,940°±20°C
80 Pt-20 Rh	1,890°C	do [13]	1,905°±20°C
90 Pt-10 Rh	1,845°C	do [13]	1,845°±20°C
100 Pt	1,776°C	do [14]	1,773.5°±1°C

[13] J. S. Acken, BS J. Research **12**, 249 (1934) RP650.
[14] W. F. Roeser, F. R. Caldwell, and H. T. Wensel, BS J. Research **6**, 1119 (1931) RP326.

VI. RESULTS

The results are summarized as follows:

Test	1	2	3	4	5	6	7
Al_2O_3	*A*	*C*	*C*	*C*	*A*	*B*	*B*
Pyrometer	*D*	*D*	*D*	*E*	*E*	*F*	*F*
Heating rate, °C/min	1	1	5	3	1	1.7	2
Melting point, °C	2,000	1,990	2,010	2,000	2,010	1,997	1,995

The melting point was taken as the temperature at which the corners of the specimen were seen to become rounded. Heating slowly (1°/min) during tests 1 and 5 beyond the temperature at which melting started caused an appreciable flow of the molten Al_2O_3 when the temperature reached 2,025°C and 2,035°C, respectively.

ThO_2 was selected for all of the parts making up the heating chamber because it is believed to have a very low vapor pressure at the temperatures attained in this work. Nevertheless, to determine if the alumina had been contaminated during the heating, the specimens from tests 1 and 2 were analyzed in the Spectroscopy Section of the National Bureau of Standards, and specimens from tests 6 and 7 were returned for quantitative spectrographic analysis to the concern which had supplied alumina *B*.

All the spectrographic analyses of the tested specimens indicated an appreciable "pickup" of impurities from the furnace atmosphere. This contamination was determined to be 1.1 percent of the top portion of the specimen and 1.0 percent of the bottom portion. It apparently was composed of about 0.5 silica and 0.3 magnesia, with nickel and iron making up the bulk of the remainder. The furnace parts shown in figure 1 had been used only for these melting-point tests of alumina, and consequently the contaminating oxides must have found their

way as vapors into the heating chamber from the outer and relatively colder parts of the furnace.

It is possible that the contaminaton was concentrated in the outer portions of the specimens from aluminas *A* and *B*, in which case it could have had a marked effect on the melting behavior, and the beginning of melting noted at 2,000°±10° C may have been the formation of a rather impure liquid at the surface. In support of this possibility, it was noted that specimens of alumina *C*, which were porous and therefore susceptible to contamination throughout the mass, melted sharply and uniformly, rather than beginning at the surface. Available information indicates that the two principal impurities, silica and magnesia, would lower the temperature at which melting would begin. Although the average value of 2,000° C obtained for the beginning of melting of the alumina used in the present investigation is considered accurate to ±10 degrees centigrade, the melting point of pure alumina may be slightly higher. However, it seems likely that the generally accepted value of 2,050° C is too high, and that a more correct value will be in the range 2,000° to 2,030° C.

VII. CONCLUSION

As a result of the observations reported in this paper, it is believed that the melting point of alpha–Al_2O_3 is within the range 2,000° to 2,030° C, and that a more accurate determination of the true value must involve prevention of contamination of the alumina specimen by vapors of other elements in the furnace atmosphere.

WASHINGTON, February 23, 1945.

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U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1650

Part of Journal of Research of the National Bureau of Standards, Volume 34, April 1945

HEATS AND FREE ENERGIES OF FORMATION OF THE PARAFFIN HYDROCARBONS, IN THE GASEOUS STATE, TO 1,500° K[1]

By Edward J. Prosen, Kenneth S. Pitzer,[2] and Frederick D. Rossini

ABSTRACT

Values are presented for the heats of formation and the free energies of formation, from solid carbon (graphite) and gaseous hydrogen, of all the normal paraffin hydrocarbons and of the isomeric paraffins from the butanes through the octanes, in the gaseous state, to 1,500° K.

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I. INTRODUCTION

This paper presents new values for the heats and free energies of formation, from solid carbon (graphite) and gaseous hydrogen, of each of the 40 paraffin hydrocarbons from methane through the octanes, and of the higher normal paraffins, in the gaseous state, to 1,500° K.

II. UNIT OF ENERGY AND MOLECULAR WEIGHTS

The unit of energy used in this paper is the conventional thermochemical calorie defined as follows [1].[3]

1 calorie=4.1833 international (NBS) joules.

The molecular weights were calculated from the values given in the 1941 table of International Atomic Weights [2].

[1] This investigation was performed at the National Bureau of Standards jointly by the Thermochemical Laboratory and the American Petroleum Institute Research Project 44 on the "Collection and Analysis of Data on the Properties of Hydrocarbons."

[2] Consultant to the American Petroleum Institute Research Project 44 Professor of Chemistry, University of California, Berkeley, Calif.

[3] Figures in brackets indicate the literature references at the end of this paper.

III. METHOD OF CALCULATION

Values of $\Delta Hf°_0$, the increment in heat content for the reaction of forming the given hydrocarbon in the gaseous state, from the elements carbon (solid, graphite) and hydrogen (gas), with the reactants and the product in their appropriate thermodynamic standard states, at 0° K, were calculated by combining values of $\Delta Hf°_{298.16}$ with values of $H°_{298.16}-H°_0$ for the appropriate compounds, by means of the relation [4]

$$\Delta Hf°_0=\Delta Hf°_{298.16}-\Delta(H°_{298.16}-H°_0), \tag{1}$$

where the last term on the right is the value of $H°_{298.16}-H°_0$ (the heat content at 25° C less that at 0° K) for 1 mole of the gaseous hydrocarbon less that of n moles of solid carbon (graphite) and $(n+1)$ moles of gaseous hydrogen (the molecular formula of the hydrocarbon being C_nH_{2n+2}).

Values of $\Delta Hf°$ for the other temperatures were then systematically calculated by means of the relation

$$\Delta Hf°=\Delta Hf°_0+\Delta(H°-H°_0). \tag{2}$$

Values of $\Delta Ff°$, the increment in free energy for the reaction of forming the given hydrocarbon in the gaseous state, from the elements carbon (solid, graphite) and hydrogen (gas), with the reactants and the product in their appropriate thermodynamic standard states at the given temperature, were calculated by combining values of $\Delta Hf°_0$ with appropriate values of $(F°-H°_0)/T$, the free-energy function, by means of the relation

$$\Delta Ff°=\Delta Hf°_0+T\Delta(F°-H°_0)/T, \tag{3}$$

where the last term on the right is the value of the product of the absolute temperature and $\Delta(F°-H°_0)/T$, the free energy at the given temperature less the heat content at 0° K, divided by the absolute temperature, for 1 mole of the gaseous hydrocarbon less that of n moles of solid carbon (graphite) and $(n+1)$ moles of gaseous hydrogen (the molecular formula of the hydrocarbon being C_nH_{2n+2}).

IV. DATA USED IN THE CALCULATIONS

The data used in the calculations include the following:

Values of the heat of formation, $\Delta Hf°$, for the gaseous hydrocarbons at 25° C are taken from reference [4].

Values of the heat content at a given temperature less that at 0° K, $H°-H°_0$, and of the free-energy function, $(F°-H°_0)/T$, for the gaseous hydrocarbons, are taken from the following sources: For methane, from reference [5]; for ethane, propane, n-butane, n-pentane, n-hexane, n-heptane, n-octane, and the higher normal paraffins, from refer-

[4] The usual convention is followed of letting the subscript denote the absolute temperature. The superscript denotes the thermodynamic standard state. See reference [3].

ence [6]; for isobutane, isopentane, and neopentane, from reference [7]; for the difference between *n*-hexane and its isomers and between *n*-heptane and its isomers, from reference [8]; for the isomeric octanes, from references [7] and [9]. Values of the foregoing properties for several of the intermediate temperatures were calculated by W. J. Taylor of this Bureau in connection with the work of the American Petroleum Institute Research Project 44.

V. RESULTS OF THE CALCULATIONS

The resulting values [5] of the heat of formation, $\Delta Hf°$, are given in table 1. The resulting values [5] of the free energy of formation, $\Delta Ff°$, are given in table 2.

[5] The uncertainty in the values for 2,3-dimethylhexane may be several times that for the other isomeric octanes [4].

TABLE 1.—*Values of the heats of formation of the paraffin hydrocarbons in the gaseous state to 1,500° K*

Compound (gas)	Temperature in °K														
	0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
	$\Delta Hf°$ in kcal/mole														
Methane	−15.987	−17.889	−17.903	−18.629	−19.302	−19.893	−20.401	−20.823	−21.166	−21.43	−21.65	−21.79	−21.92	−22.00	−22.06
Ethane	−16.517	−20.236	−20.258	−21.419	−22.437	−23.28	−23.98	−24.53	−24.97	−25.28	−25.50	−25.64	−25.72	−25.75	−25.73
Propane	−19.482	−24.820	−24.848	−26.358	−27.622	−28.66	−29.49	−30.12	−30.58	−30.90	−31.09	−31.16	−31.19	−31.14	−31.06
n-Butane	−23.332	−29.812	−29.847	−31.629	−33.128	−34.33	−35.28	−36.00	−36.54	−36.88	−37.06	−37.11	−37.05	−36.95	−36.79
2-Methylpropane	−24.602	−31.452	−31.489	−33.303	−34.783	−35.97	−36.91	−37.61	−38.10	−38.42	−38.57	−38.58	−38.54	−38.43	−38.28
n-Pentane	−27.27	−35.00	−35.04	−37.12	−38.86	−40.25	−41.34	−42.16	−42.75	−43.10	−43.26	−43.27	−43.18	−42.99	−42.74
2-Methylbutane	−28.66	−36.92	−36.96	−39.07	−40.78	−42.12	−43.17	−43.94	−44.47	−44.80	−44.92	−44.88	−44.78	−44.58	−44.36
2, 2-Dimethylpropane	−31.30	−39.67	−39.71	−41.77	−43.42	−44.67	−45.63	−46.29	−46.73	−46.96	−47.01	−46.90	−46.70	−46.42	−46.12
n-Hexane	−30.98	−39.96	−40.01	−42.38	−44.36	−45.93	−47.15	−48.06	−48.71	−49.07	−49.23	−49.19	−49.04	−48.78	−48.47
2-Methylpentane	−32.03	−41.66	−41.71	−44.04	−45.92	−47.35	−48.43	−49.23	−49.84	−50.27					
3-Methylpentane	−31.36	−41.02	−41.07	−43.40	−45.27	−46.68	−47.73	−48.49	−49.05	−49.40					
2,2-Dimethylbutane	−34.52	−44.35	−44.40	−46.76	−48.64	−50.03	−51.05	−51.75	−52.22	−52.46					
2,3-Dimethylbutane	−32.82	−42.49	−42.54	−44.81	−46.59	−47.93	−48.92	−49.65	−50.23	−50.65					
n-Heptane	−34.65	−44.89	−44.94	−47.60	−49.83	−51.58	−52.93	−53.94	−54.63	−55.01	−55.15	−55.08	−54.88	−54.55	−54.16
2-Methylhexane	−35.77	−46.60	−46.66	−49.30	−51.45	−53.09	−54.33	−55.25	−55.91	−56.33					
3-Methylhexane	−34.96	−45.96	−46.02	−48.71	−50.90	−52.58	−53.84	−54.77	−55.42	−55.82					
3-Ethylpentane	−34.10	−45.34	−45.40	−48.15	−50.40	−52.12	−53.43	−54.41	−55.11	−55.56					
2,2-Dimethylpentane	−38.00	−49.29	−49.35	−52.02	−54.14	−55.72	−56.87	−57.69	−58.25	−58.56					
2,3-Dimethylpentane	−36.29	−47.62	−47.68	−50.39	−52.56	−54.21	−55.43	−56.35	−57.01	−57.45					
2,4-Dimethylpentane	−36.98	−48.30	−48.36	−51.02	−53.13	−54.70	−55.85	−56.69	−57.27	−57.64					
3,3-Dimethylpentane	−36.92	−48.17	−48.23	−50.88	−52.98	−54.54	−55.67	−56.46	−56.98	−57.28					
2,2,3-Trimethylbutane	−37.57	−48.96	−49.02	−51.64	−53.69	−55.19	−56.25	−57.01	−57.52	−57.83					
n-Octane	−38.33	−49.82	−49.88	−52.83	−55.30	−57.23	−58.71	−59.81	−60.57	−60.96	−61.08	−60.97	−60.71	−60.31	−59.86
2-Methylheptane	−39.42	−51.50	−51.56	−54.49	−56.87	−58.67	−60.04	−61.13	−61.91	−62.19					
3-Methylheptane	−38.64	−50.82	−50.88	−53.84	−56.23	−58.03	−59.40	−60.49	−61.27	−61.57					
4-Methylheptane	−38.43	−50.69	−50.75	−53.73	−56.13	−57.97	−59.39	−60.47	−61.23	−61.55					
3-Ethylhexane	−37.71	−50.40	−50.46	−53.59	−56.10	−58.04	−59.53	−60.64	−61.42	−61.81					
2,2-Dimethylhexane	−41.23	−53.71	−53.77	−56.72	−59.06	−60.85	−62.16	−63.02	−63.66	−63.96					
2,3-Dimethylhexane	−38.76	−51.13	−51.19	−54.08	−56.26	−57.88	−59.11	−60.10	−60.83	−61.16					
2,4-Dimethylhexane	−39.74	−52.44	−52.51	−55.50	−57.92	−59.72	−61.06	−62.10	−62.86	−63.23					
2,5-Dimethylhexane	−40.61	−53.21	−53.27	−56.24	−58.58	−60.33	−61.66	−62.70	−63.45	−63.77					
3,3-Dimethylhexane	−39.90	−52.61	−52.68	−55.65	−58.03	−59.78	−61.04	−61.93	−62.54	−62.84					
3,4-Dimethylhexane	−38.82	−50.91	−50.97	−53.81	−56.05	−57.71	−58.98	−60.05	−60.82	−61.01					
2-Methyl-3-ethylpentane	−37.95	−50.48	−50.54	−53.46	−55.77	−57.52	−58.87	−59.95	−60.70	−60.93					
3-Methyl-3-ethylpentane	−38.68	−51.38	−51.45	−54.32	−56.65	−58.42	−59.74	−60.55	−61.18	−61.29					
2,2,3-Trimethylpentane	−39.77	−52.61	−52.68	−55.62	−57.92	−59.63	−60.89	−61.82	−62.43	−62.63					
2,2,4-Trimethylpentane	−40.73	−53.57	−53.64	−56.58	−58.88	−60.59	−61.85	−62.78	−63.39	−63.59					
2,3,3-Trimethylpentane	−39.01	−51.73	−51.80	−54.72	−56.96	−58.66	−59.93	−60.92	−61.58	−61.82					

3,4-Dimethylhexane	−38.52	−50.91	−50.97	−53.81	−56.05	−57.71	−58.98	−60.05	−60.82	−61.01	----	----	----	----	----
2-Methyl-3-ethylpentane	−37.96	−50.48	−50.54	−53.46	−55.77	−57.52	−58.87	−59.95	−60.70	−60.93	----	----	----	----	----
3-Methyl-3-ethylpentane	−38.68	−51.38	−51.45	−54.32	−56.65	−58.42	−59.74	−60.65	−61.18	−61.29	----	----	----	----	----
2,2,3-Trimethylpentane	−39.77	−52.61	−52.68	−55.62	−57.92	−59.63	−60.89	−61.82	−62.43	−62.63	----	----	----	----	----
2,2,4-Trimethylpentane	−40.73	−53.57	−53.64	−56.58	−58.88	−60.59	−61.85	−62.78	−63.39	−63.59	----	----	----	----	----
2,3,3-Trimethylpentane	−39.01	−51.73	−51.80	−54.72	−56.98	−58.66	−59.93	−60.92	−61.56	−61.62	----	----	----	----	----
2,3,4-Trimethylpentane	−39.12	−51.97	−52.04	−54.97	−57.18	−58.83	−60.11	−61.17	−61.91	−62.03	----	----	----	----	----
2,2,3,3-Tetramethylbutane	−41.09	−53.99	−54.06	−56.96	−59.14	−60.65	−61.70	−62.51	−63.02	−63.03	----	----	----	----	----
n-Nonane	−42.00	−54.74	−54.81	−58.05	−60.76	−62.88	−64.49	−65.68	−66.50	−66.90	−67.01	−66.85	−66.54	−66.07	−65.55
n-Decane	−45.67	−59.67	−59.74	−63.28	−66.23	−68.53	−70.27	−71.55	−72.42	−72.84	−72.94	−72.74	−72.37	−71.82	−71.24
n-Undecane	−49.34	−65.60	−64.67	−68.50	−71.69	−74.17	−76.04	−77.42	−78.35	−78.78	−78.87	−78.63	−78.20	−77.58	−76.93
n-Dodecane	−53.02	−69.52	−69.60	−73.72	−77.16	−79.82	−81.82	−83.29	−84.28	−84.72	−84.79	−84.51	−84.03	−83.34	−82.63
n-Tridecane	−56.69	−74.45	−74.53	−78.94	−82.62	−85.47	−87.60	−89.17	−90.20	−90.66	−90.72	−90.40	−89.86	−89.10	−88.32
n-Tetradecane	−60.36	−79.38	−79.46	−84.17	−88.09	−91.12	−93.38	−95.04	−96.13	−96.60	−96.65	−96.28	−95.69	−94.86	−94.01
n-Pentadecane	−64.04	−84.31	−84.39	−89.39	−93.55	−96.77	−99.16	−100.91	−102.06	−102.54	−102.57	−102.17	−101.52	−100.61	−99.70
n-Hexadecane	−67.71	−89.23	−89.33	−94.61	−99.02	−102.41	−104.93	−106.78	−107.99	−108.48	−108.50	−108.06	−107.35	−106.37	−105.39
n-Heptadecane	−71.38	−94.15	−94.26	−99.84	−104.48	−108.06	−110.71	−112.65	−113.91	−114.42	−114.43	−113.94	−113.19	−112.13	−111.08
n-Octadecane	−75.06	−99.08	−99.19	−105.06	−109.95	−113.71	−116.49	−118.52	−119.84	−120.37	−120.35	−119.83	−119.02	−117.89	−116.78
n-Nonadecane	−78.73	−104.00	−104.12	−110.28	−115.41	−119.36	−122.27	−124.39	−125.77	−126.31	−126.28	−125.71	−124.85	−123.64	−122.47
n-Eicosane	−82.40	−108.93	−109.05	−115.50	−120.88	−125.01	−128.04	−130.26	−131.69	−132.25	−132.21	−131.60	−130.68	−129.40	−128.16
Δ per CH_2	−3.673	−4.926	−4.931	−5.223	−5.465	−5.648	−5.778	−5.871	−5.927	−5.941	−5.927	−5.886	−5.830	−5.758	−5.692

TABLE 2.—*Values of the free energies of formation of the paraffin hydrocarbons in the gaseous state to 1,500 °K*

Compound (gas)	Temperature in °K														
	0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
	$\Delta Ff°$ in kcal/mole														
Methane	−15.987	−12.140	−12.105	−10.048	−7.841	−5.49	−3.05	−0.55	2.01	4.61	7.22	9.85	12.50	15.14	17.79
Ethane	−16.517	−7.860	−7.785	−3.447	1.168	5.97	10.90	15.92	21.00	26.13	31.28	36.45	41.62	46.79	51.99
Propane	−19.482	−5.614	−5.541	1.191	8.230	15.50	22.93	30.45	38.05	45.68	53.34	61.01	68.68	76.35	84.08
n-Butane	−23.332	−3.754	−3.595	5.435	14.868	24.59	34.50	44.50	54.59	64.71	74.87	85.05	95.25	105.42	115.61
2-Methylpropane	−24.602	−4.296	−4.127	5.273	15.088	25.18	35.44	45.82	56.29	66.79	77.32	87.86	98.39	108.90	119.44
n-Pentane	−27.27	−1.96	−1.76	9.66	21.57	33.79	46.22	58.77	71.41	84.10	96.81	109.55	122.30	135.01	147.75
2-Methylbutane	−28.66	−3.50	−3.38	8.26	20.29	32.66	45.19	57.84	70.62	83.41	96.23	109.07	121.89	134.68	147.53
2,2-Dimethylpropane	−31.30	−3.64	−3.42	8.99	21.89	35.08	48.46	61.93	75.49	89.08	102.68	116.27	129.88	143.44	157.00
n-Hexane	−30.96	0.05	0.30	14.11	28.46	43.18	58.13	73.21	88.40	103.64	118.90	134.19	149.48	164.75	180.04
2-Methylpentane	−32.03	−0.96	−0.71	13.25	27.79	42.72	57.88	73.15	88.51	103.86	.....	.....	.....	.....	.....
3-Methylpentane	−31.36	−0.29	−0.04	13.94	28.50	43.45	58.62	73.89	89.23	104.53	.....	.....	.....	.....	.....
2,2-Dimethylbutane	−34.52	−2.35	−2.09	12.30	27.30	42.69	58.29	73.97	89.71	105.37	.....	.....	.....	.....	.....
2,3-Dimethylbutane	−32.82	−0.73	−0.47	13.81	28.67	43.92	59.38	74.94	90.57	106.18	.....	.....	.....	.....	.....
n-Heptane	−34.65	2.09	2.38	18.58	35.39	52.60	70.08	87.70	105.43	123.22	141.02	158.85	176.69	194.50	212.38
2-Methylhexane	−35.77	0.98	1.27	17.61	34.60	52.01	69.67	87.47	105.33	123.18	.....	.....	.....	.....	.....
3-Methylhexane	−34.96	1.10	1.39	17.57	34.40	51.68	69.21	86.87	104.59	122.29	.....	.....	.....	.....	.....
3-Ethylpentane	−34.10	2.59	2.88	19.36	36.52	54.15	72.06	90.09	108.19	126.25	.....	.....	.....	.....	.....
2,2-Dimethylpentane	−38.00	0.09	0.39	17.33	34.95	53.01	71.33	89.73	108.18	126.55	.....	.....	.....	.....	.....
2,3-Dimethylpentane	−36.29	0.16	0.45	16.83	33.90	51.43	69.24	87.17	105.18	123.16	.....	.....	.....	.....	.....
2,4-Dimethylpentane	−36.98	0.72	1.02	17.81	35.28	53.19	71.37	89.66	107.99	126.27	.....	.....	.....	.....	.....
3,3-Dimethylpentane	−36.92	0.63	0.93	17.64	35.02	52.84	70.92	89.10	107.34	125.53	.....	.....	.....	.....	.....
2,2,3-Trimethylbutane	−37.57	0.76	1.06	18.06	35.75	53.87	72.24	90.72	109.23	127.66	.....	.....	.....	.....	.....
n-Octane	−38.33	4.14	4.47	23.06	42.32	62.03	82.03	102.17	122.45	142.79	163.14	183.51	203.90	224.26	244.71
2-Methylheptane	−39.42	3.06	3.39	22.14	41.58	61.47	81.63	101.88	122.27	142.83	.....	.....	.....	.....	.....
3-Methylheptane	−38.64	3.29	3.62	22.21	41.50	61.27	81.31	101.44	121.68	142.07	.....	.....	.....	.....	.....
4-Methylheptane	−38.43	4.00	4.34	23.12	42.62	62.61	82.88	103.23	123.68	144.26	.....	.....	.....	.....	.....
3-Ethylhexane	−37.71	3.95	4.28	22.94	42.39	62.37	82.64	102.98	123.42	143.98	.....	.....	.....	.....	.....
2,2-Dimethylhexane	−41.23	2.56	2.91	22.18	42.20	62.71	83.48	104.30	125.21	146.27	.....	.....	.....	.....	.....
2,3-Dimethylhexane	−39.74	2.80	3.14	22.05	41.72	61.89	82.32	102.84	123.43	144.07	.....	.....	.....	.....	.....
2,4-Dimethylhexane	−39.74	2.80	3.14	22.05	41.75	62.09	82.69	103.41	124.20	144.99	.....	.....	.....	.....	.....
2,5-Dimethylhexane	−40.61	2.59	2.84	21.92	41.75	62.20	82.85	103.47	124.16	144.93	145.76	.....	.....	.....	.....
3,3-Dimethylhexane	−39.90	3.17	3.51	22.63	42.50	62.85	83.47	104.16	124.93	145.76	.....	.....	.....	.....	.....
3,4-Dimethylhexane	−38.52	4.97	5.31	24.42	44.27	64.57	85.12	105.75	126.49	147.35	.....	.....	.....	.....	.....
3-Methyl-3-ethylpentane	−37.96	5.08	5.43	24.47	44.24	64.47	84.96	105.52	126.21	147.09	.....	.....	.....	.....	.....

2,3-Dimethylhexane	−38.76	4.23	4.57	23.53	43.16	63.27	83.54	104.02	124.63	145.37					
2,4-Dimethylhexane	−39.74	2.80	3.14	22.05	41.72	61.89	82.32	102.84	123.43	144.07					
2,5-Dimethylhexane	−40.61	2.50	2.84	21.92	41.75	62.08	82.69	103.41	124.20	144.99					
3,3-Dimethylhexane	−39.80	3.17	3.51	22.63	42.50	62.35	83.47	104.16	124.93	145.76					
3,4-Dimethylhexane	−38.52	4.97	5.31	24.42	44.27	64.57	85.12	105.75	126.49	147.35					
2-Methyl-3-ethylpentane	−37.96	5.08	5.43	24.47	44.24	64.47	84.96	105.52	126.21	147.09					
3-Methyl-3-ethylpentane	−38.68	4.76	5.11	24.32	44.30	64.77	85.48	106.22	127.05	148.01					
2,2,3-Trimethylpentane	−39.77	4.09	4.44	23.82	43.98	64.63	85.54	106.52	127.57	148.68					
2,2,4-Trimethylpentane	−40.73	3.13	3.48	22.86	43.02	63.67	84.58	105.56	126.61	147.72					
2,3,3-Trimethylpentane	−39.01	4.52	4.86	24.09	44.08	64.55	85.30	106.10	126.98	147.90					
2,3,4-Trimethylpentane	−39.12	4.32	4.67	23.89	43.89	64.37	85.11	105.94	126.84	147.80					
2,2,3,3-Tetramethylbutane	−41.09	4.88	5.24	25.34	46.19	67.47	88.97	110.52	132.19	154.05					
n-Nonane	−42.00	6.18	6.56	27.54	49.25	71.46	93.96	116.66	139.48	162.37	184.20	208.18	231.12	254.03	277.04
n-Decane	−45.67	8.23	8.65	32.01	56.18	80.89	105.93	131.14	156.51	181.95	205.26	232.85	258.33	283.79	309.37
n-Undecane	−49.34	10.28	10.74	36.49	63.11	90.31	117.88	145.63	173.54	201.53	226.32	257.52	285.54	313.55	341.70
n-Dodecane	−53.02	12.33	12.83	40.97	70.04	99.74	129.83	160.11	190.57	221.11	247.38	282.19	312.76	343.32	374.03
n-Tridecane	−56.69	14.37	14.92	45.45	76.97	109.17	141.78	174.59	207.60	240.69	268.45	306.86	339.97	373.08	406.36
n-Tetradecane	−60.36	16.42	17.01	49.93	83.90	118.60	153.73	189.08	224.63	260.26	289.51	331.52	367.19	402.85	438.69
n-Pentadecane	−64.04	18.47	19.10	54.41	90.83	128.03	165.68	203.56	241.66	279.84	310.57	356.19	394.40	432.61	471.02
n-Hexadecane	−67.71	20.52	21.19	58.89	97.76	137.46	177.63	218.04	258.69	299.42	331.63	380.86	421.62	462.38	503.36
n-Heptadecane	−71.38	22.56	23.27	63.36	104.69	146.88	189.58	232.53	275.72	319.00	352.69	405.53	448.83	492.14	535.69
n-Octadecane	−75.06	24.61	25.36	67.84	111.62	156.31	201.53	247.01	292.75	338.58	373.75	430.20	476.05	521.90	568.02
n-Nonadecane	−78.73	26.66	27.45	72.32	118.55	165.74	213.48	261.49	309.78	358.16	394.81	454.86	503.26	551.67	600.35
n-Eicosane	−82.40	28.71	29.54	76.80	125.48	175.17	225.43	275.98	326.81	377.74	415.87	479.53	530.48	581.43	632.68
Δ per CH_2	−3.673	2.048	2.090	4.479	6.931	9.428	11.951	14.484	17.029	19.579	21.061	24.668	27.215	29.764	32.331

Figure 1 is a plot that shows the thermodynamic stability, per carbon atom and with respect to the elements solid carbon (graphite) and gaseous hydrogen, of the normal paraffin hydrocarbons in the gaseous state as a function of the temperature. This plot shows the thermodynamic stability, per carbon atom, with respect to the ele-

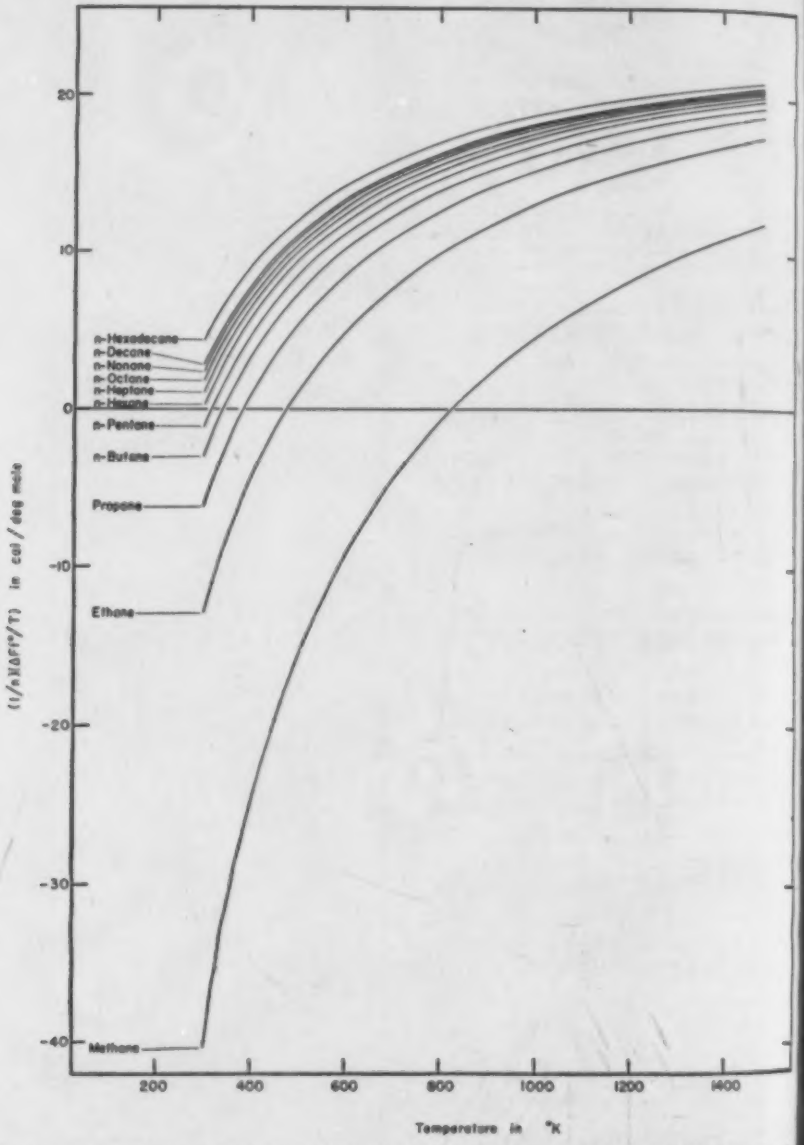

FIGURE 1.—*Thermodynamic stability of the normal paraffin hydrocarbons in the gaseous state as a function of temperature.*

The scale of ordinates gives the value of $(1/n)\ (\Delta F)^\circ/T)$ in calories per degree mole, where n is the number of carbon atoms per molecule, T is the absolute temperature in degrees Kelvin, and $\Delta F)^\circ$ is the standard free energy of formation of the hydrocarbon from the elements, solid carbon (graphite) and gaseous hydrogen, as given in table 2. The scale of abecissas gives the temperature in degrees Kelvin.

ments, of the normal paraffin hydrocarbons in the gaseous state. Points below the zero line indicate that the gaseous hydrocarbon in its standard state has a thermodynamic tendency to be formed from solid carbon (graphite) and gaseous hydrogen in their respective standard states.

Plots showing the relative stability of *n*-butane and isobutane, the 3 pentanes, the 5 hexanes, the 9 heptanes, and the 18 octanes, are given in references [9 and 10].

VI. REFERENCES

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